THE PHYSICAL SOCIETY OF LONDON.

PROCEEDINGS.

VOLUME 36.—PART 1.
DECEMBER 15, 1923.

Price to Non-Fellows, **6s.** *net, post free* **6/3.**
Annual Subscription, **30/-** *post free, payable in advance.*

Published Bi-Monthly from December to August.

LONDON:
FLEETWAY PRESS, LTD.,
9 DANE STREET, HIGH HOLBORN, W.C.1.

1923.

THE PHYSICAL SOCIETY OF LONDON.

1923-24.

OFFICERS AND COUNCIL.

President.

ALEXANDER RUSSELL, M.A., D.Sc.

Vice-Presidents.

(WHO HAVE FILLED THE OFFICE OF PRESIDENT)

SIR OLIVER J. LODGE, D.Sc., F.R.S.
SIR RICHARD GLAZEBROOK, K.C.B., D.Sc., F.R.S.
C. CHREE, Sc.D., LL.D., F.R.S.
PROF. H. L. CALLENDAR, M.A., LL.D., F.R.S.
SIR ARTHUR SCHUSTER, PH.D., Sc.D., F.R.S.
SIR J. J. THOMSON, O.M., D.Sc., F.R.S.
PROF. C. VERNON BOYS, F.R.S.
PROF. C. H. LEES, D.Sc., F.R.S.
PROF. SIR W. H. BRAGG, K.B.E., M.A., F.R.S.

Vice-Presidents.

E. H. BARTON, D.Sc., F.R.S.
PROF. T. MATHER, F.R.S.
T. SMITH, B.A.
C. R. DARLING, F.I.C.

Secretaries.

PROF. A. O. RANKINE, D.Sc.
Imperial College of Science and Technology, South Kensington, S.W.7.

D. OWEN, B.A., D.Sc.
62, *Wellington Road, Enfield, Middlesex.*

Foreign Secretary.

SIR ARTHUR SCHUSTER, PH.D., Sc.D., F.R.S.

Treasurer.

W. R. COOPER, M.A., B.Sc.
82, *Victoria Street, S.W.1.*

Librarian.

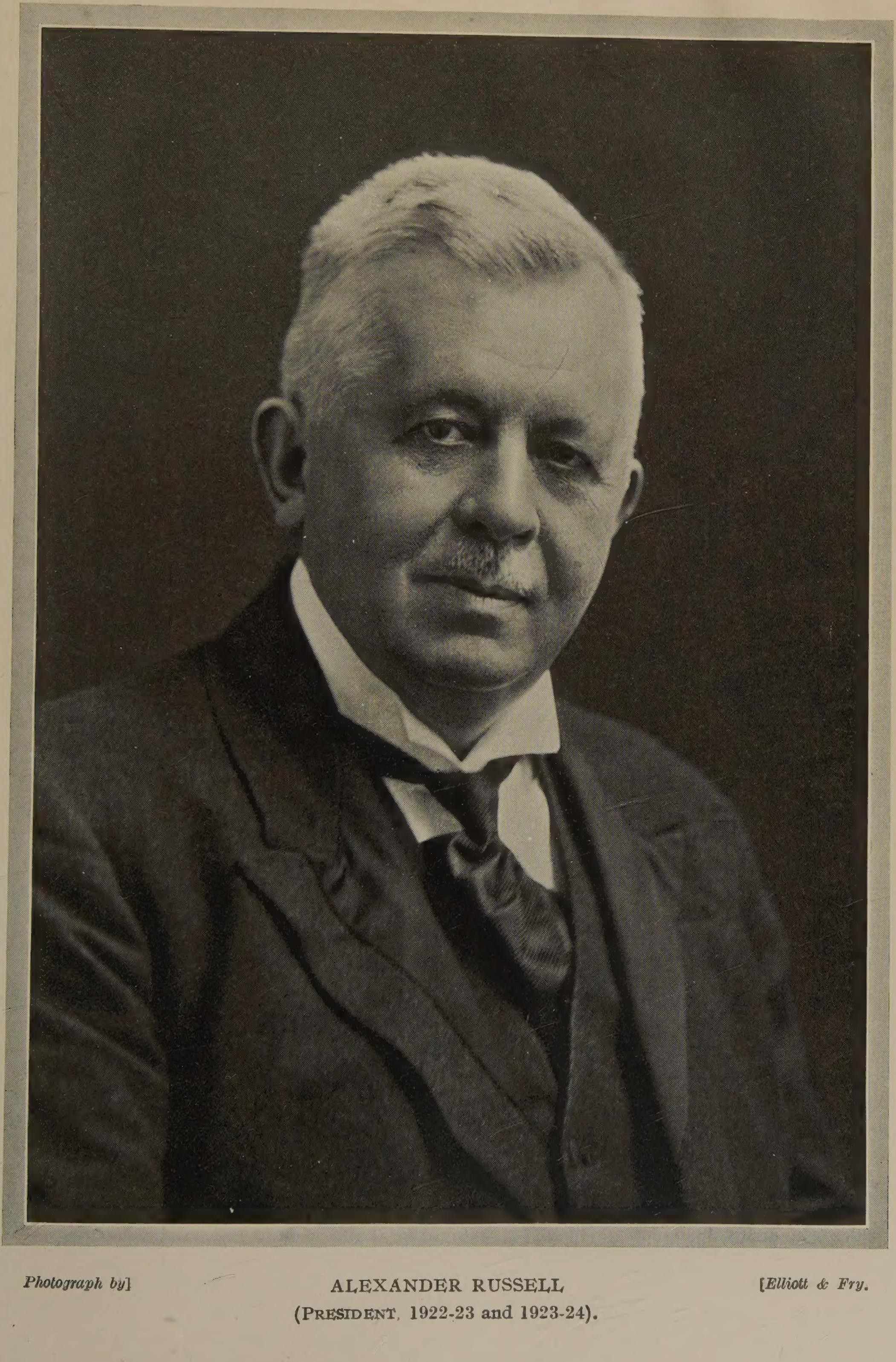
J. H. BRINKWORTH, B.Sc.
Imperial College of Science and Technology.

Other Members of Council.

G. B. BRYAN, D.Sc.
PROF. C. L. FORTESCUE, O.B.E.
J. GUILD, A.R.C.Sc., D.I.C.
F. L. HOPWOOD, D.Sc.
E. A. OWEN, B.A., D.Sc.
R. W. PAUL.
E. H. RAYNER, M.A., D.Sc.
W. S. TUCKER, D.Sc.
J. H. VINCENT, D.Sc., M.A.

Assistant Secretary (Publications).

CAPT. C. W. HUME, M.C., B.Sc.
14, *The Hawthorns, Finchley, N.3.*



Photograph by] ALEXANDER RUSSELL [*Elliott & Fry.*

(PRESIDENT, 1922-23 and 1923-24).

THE EXCITATION AND IONIZATION POTENTIALS OF GASES AND VAPOURS.

By FRANK HORTON, *Sc.D., F.R.S.*

(A report of a lecture delivered before the Society on *June* 22, 1923.)

THE phenomenon of ionization by collision has long been recognised as an important factor in the process of the conduction of electricity through gases, but our knowledge of the subject has advanced with remarkable rapidity in the last few years as a result of the development by Bohr of the nuclear theory of atomic structure. When a moving electron collides with an atom there may, or there may not, be a considerable transfer of energy between the two. Whether such a transfer takes place or not depends mainly on the kinetic energy of the colliding electron. If this is greater than a certain minimum value such a transference of energy may take place, but for energies below this critical value the transfer of energy on collision, at least in the case of the monatomic gases and vapours, is very small, and the impact may be said to be an elastic one. In the case of the inelastic collisions some of the energy of the colliding electron is absorbed by the atom, and this absorption of energy causes either the ionization of the atom, or on Bohr's theory, the displacement of an outer electron of the atomic system without completely removing it from the atom. The minimum difference of potential through which an electron must fall in order to acquire sufficient energy to enable it to ionize a normal atom on collision with it is called the *ionization potential* for the atom. Similarly the minimum potential difference which will give to the colliding electron sufficient energy to enable it to displace one of the outer electrons of the atomic structure from its normal orbit to some other orbit within the atom is termed the *excitation potential* for the atom.

The recognition of the possibility of the existence of excitation potentials is due to Bohr, and arises directly from his theory of atomic structure. The outlines of this theory may perhaps best be understood by a consideration of the application of it to the case of the simplest atom—that of hydrogen. The fundamental conceptions of Bohr's theory of the structure of the hydrogen atom may be summarised briefly as follows :—

1. The hydrogen atom in its normal condition consists of a single electron revolving in a circular orbit round a positively charged nucleus.
2. In the excited condition the possible orbits of the electron are concentric circles of larger diameter than the normal orbit, and ellipses with the nucleus at one focus. The possible orbits are limited by the theory to those with which certain definite amounts of energy are associated. This energy must be equal to

$$a \ constant \quad - \quad \frac{R\,h\,c}{n^2}$$

where R is Rydberg's constant, h is Planck's constant, c is the velocity of light, and n is an integer known as the principal quantum numbe of the orbit.

3. Contrary to the principles of ordinary electrodynamics, no emission o radiation occurs while the electron revolves in its orbit. Radiation i only emitted when, after the atom has been "excited" or ionized an electron falls from an outer orbit to an inner orbit of smaller energ value. The energy emitted during such a transition is in the form o monochromatic radiation whose frequency (ν) is connected with th energies of the system before and after the transition by the relation $h\nu=$ E_1-E_2.

We thus see that the "excitation potential" of hydrogen is the potenti difference corresponding to the minimum amount of energy which the norma hydrogen atom can receive from an impacting electron—the energy necessary t displace the electron within the atom from the normal orbit to the orbit characterise by a higher quantum number, but which leaves the displaced electron still within th sphere of action of the nucleus. The "ionization potential" of hydrogen corre sponds to a larger amount of energy, that which, if absorbed by a normal atom, i just sufficient to separate the electron from the atom. If, after the atom has bee thus ionized, recombination occurs, the recombining electron, in its journey to th normal orbit, may pause in any of the outer orbits, and the radiation which accom panies the recombination corresponds to the jumps between orbits. Thus from large collection of recombining hydrogen atoms we get spectrum lines produce corresponding to all possible transitions.

In the case of atoms containing more than one electron we can still retain th conception of a number of outer orbits which one of the electrons of the atom ma occupy, although the energy values of these "stationary states" require mor complicated mathematical expressions for their fixation than in the simple case o the hydrogen atom. Thus, in accordance with Bohr's theory, we expect for a atoms excitation potentials which are smaller than the corresponding ionizatio potentials, and the recombination which follows the ionization of a mass of ga should give rise to all the radiations of the arc spectrum. In the case of atoms othe than hydrogen we have also the possibility of removing more than one electron, s that we may expect to have further excitation and ionization potentials correspondin to the displacement and to the removal of a second electron after the most loosel attached electron has been removed. In this way *enhanced spectra* are produced b the recombination of doubly (or trebly, &c.) ionized atoms with single electrons.

EXPERIMENTAL METHODS.

The methods by which the first critical electron energy—the excitation potenti —may be measured can be conveniently divided into two classes :—

(*a*) Those methods which depend on the detection of a loss of energy by th colliding electron.

(*b*) Those methods which depend on the detection of the radiation resultin from the collision.

That is to say, methods in which one watches for the effect of the inelastic collisio on the impacting electron, and methods in which one looks for the effect of th collisions on the bombarded atoms.

The method of testing for the occurrence of inelastic collisions has been very largely used by the American experimenters, Tate, Foote, Meggers, and Mohler. The principle of the method is as follows :—F is a glowing filament which serves as a source of electrons, G is a piece of wire gauze, and P a metal plate ; these three electrodes being enclosed in a glass apparatus which can be filled with the gas or vapour under test. Outside the apparatus the electrodes are connected to the galvanometers G_1 and G_2, and to sources of potential V_1 and V_2 as indicated in the figure. The applied potential difference V_1 serves to accelerate electrons towards the gauze G. Some of the electrons pass through the spaces between the wires of this gauze and travel on towards P, but in the space between G and P they encounter a small *retarding* potential difference V_2, usually about one or two volts. If the experiments are performed in a high vacuum, and if V_1 is gradually increased from zero in steps of a fraction of a volt, it is clear that as soon as the electrons passing through the interstices of the gauze G have, at that level, sufficient energy to carry them through the small opposing field V_2, they will reach the plate P and their collection will be indicated by the galvanometer G_1. The deflexion of this galvanometer would be expected to increase gradually as the accelerating potential V_1 is gradually raised. If, however, the apparatus contains a gas or vapour at a pressure of 1 mm. or so, the gaseous atoms are bombarded by the electron stream from F, and as V_1 is gradually raised a stage is reached when the energy of the electrons is sufficient to produce a displacement of one of the outer electrons in the bombarded atomic systems ; that is to say the excitation potential of the gas under test is reached. When this potential is attained some of the electrons in the stream from the filament lose their energy to the gaseous atoms they collide with. These electrons are therefore no longer able to pass through the retarding field V_2, but are turned back by that field and so prevented from reaching the plate P. Evidently at this stage there should be a fall in the current through the galvanometer G_1 and this fall should be accentuated as V_1 is increased a little further. Since, however, V_2 is small, and since the energy lost by the electron on collision is a perfectly definite amount (that corresponding to the excitation potential), a bombarding electron which has made an inelastic collision is soon left with sufficient energy to carry it through the opposing field and to enable it to reach the plate P, so that when V_1 is steadily raised past the

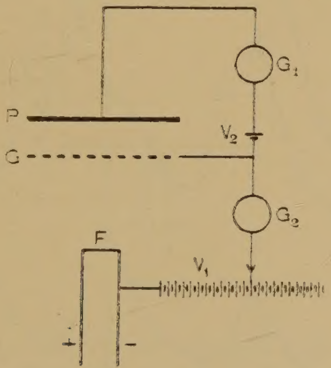


FIG. 1.

critical value the current measured by G_1 falls, and then rises again. When the values of the current measured by the galvanometer G_1 (usually called the *partial current* to distinguish it from the current measured by G_2, which is the total current from the filament) are plotted against the corresponding values of the electron energy, a gradually rising curve is obtained which shows downward bends at intervals. The commencement of each downward bend indicates the critical energy for an inelastic collision between an electron and an atom of the gas under test.

These curves are illustrated in Fig. 2, which shows partial current curves obtained by Mohler, Foote, and Meggers for mercury vapour.* The interval between the downward inflexions in curve C is 4·9 volts, which is the lowest excitation potential

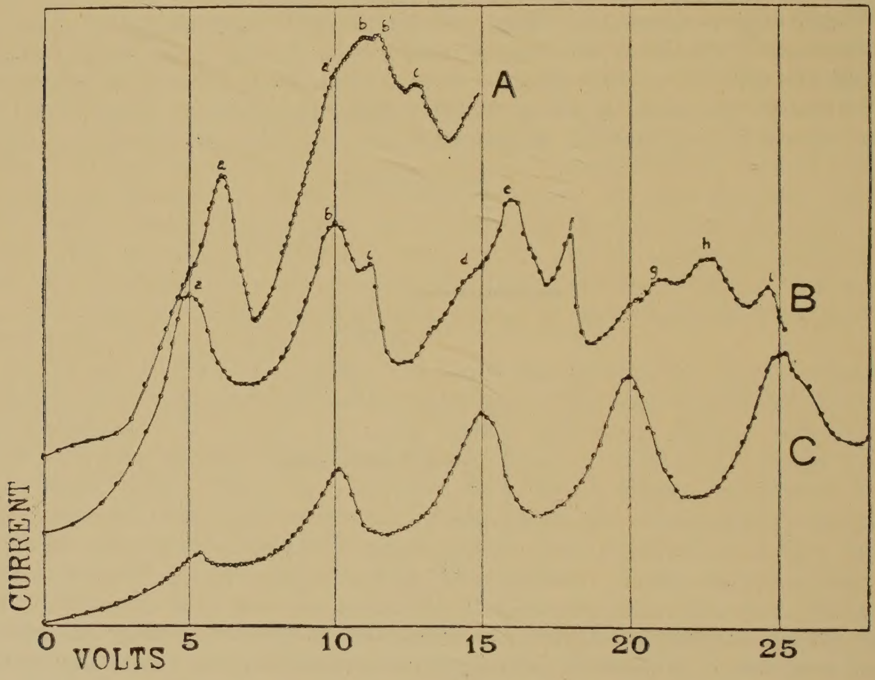


Fig. 2.

for mercury vapour. In order to obtain successive inelastic collisions as represented in this curve, the pressure of the mercury vapour must not be too low, for all the collisions indicated in the curve must occur in the space between the filament and the gauze. Over the range of voltages used the electrons from the filament are unable to attain a higher velocity than that corresponding to a fall through about 4·9 volts, for as soon as this velocity is attained it is lost by an inelastic collision. If, however, the pressure of the mercury vapour is lower, the chance of collision is smaller and many electrons from the filament reach the level of the gauze with energy corresponding to the voltage applied between the gauze and the filament. Curves representing series of observations taken under these conditions give an indication of a second excitation potential for mercury vapour at about 6·7 volts. Such a curve is shown at *B* in Fig. 2.

---

* Scientific Papers, Bureau of Standards, No. 403, p. 725 (1920).

An ingenious modification of this method has recently been employed by Hertz.* The principle of this may be gathered from Fig. 3. *F* is the glowing filament which serves as a source of electrons, *B* is a cylindrical metal box with gauze sides, and *G* is a small hole (covered with gauze) immediately above and near to the filament. The gauze sides of *B* are surrounded by a metal tube *P* which is near to the gauze, and between *B* and *P* a small difference of potential (say 0·2 volt) can be applied so as to make *B* positive to *P*. The latter electrode is connected to a delicate galvanometer which serves to detect the passage of electrons through the gauze sides of *B* against the small retarding field.

The electric field between *F* and *G* is gradually increased in steps of a fraction of a volt. Some of the electrons from the filament pass through the gauze sides of *B* to *P*, and cause the registration of a current by the galvanometer. In general, this current is only very slightly altered by varying the potential difference between *B* and *P* from 0 to 0·2 volt, for such a small opposing field stops only the very slowly-moving electrons. When, however, the energy of the bombarding electrons from *F* is raised to a critical value at which they can lose their energy on collision with the gas atoms, a much larger proportion of the electrons which pass through the gauze sides of *B* is stopped by the application of the small field between these two electrodes. In this way the attainment of a critical value for the electron energy is indicated by the detection of an increase in the number of electrons having practically zero velocity after bombarding the gas inside the cylinder *B*. Hertz has obtained very interesting results by the use of this method in experiments with the rare gases argon, helium, and neon, and he claims that it is even possible by this means to obtain separate indications of two critical voltages a small fraction of a volt apart.

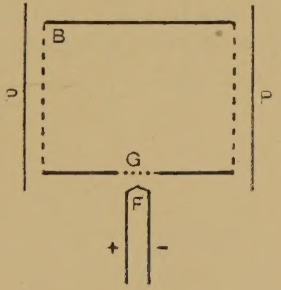


FIG. 3.

The methods of measuring the excitation potential included under the heading (*b*)—those which depend on the detection of the radiation resulting from the inelastic collisions—are most conveniently described in connection with methods of measuring the ionization potential of a gas or vapour. The first direct method of determining the ionizing potential of a gas was that devised by Lenard; and the methods now most generally used for this purpose are modifications of Lenard's method. The diagram of Fig. 4 illustrates the principle of this method. Electrons from a source

---

* Proc. Roy. Acad. Sc., Amsterdam, 25, p. 179 (1922).

F are accelerated towards a gauze *G* by a difference of potential V_1, which can be gradually increased. Those electrons which pass through the gauze enter an opposing field V_2, which is always maintained sufficiently greater than the accelerating field V_1 to prevent any of the electrons from *F* from reaching the plate *P*, which is connected to a delicate electrometer. If, however, the bombarding electron stream ionizes the gas in the space between *G* and *P*, the positive ions formed are driven by the field V_2 to the plate *P*, and cause a deflexion of the measuring instrument. It must be observed, however, that a similar deflexion of the electrometer is obtained if the bombardment of the gas results, not in ionization, but in the production of radiation from the bombarded atoms, for this radiation would act photoelectrically on the plate *P* (which is negatively charged with respect to *G*) and cause it to lose electrons. Since the electrometer connected to *P* is unable to distinguish between the loss of an electron and the gain of a positive ion, it follows that the experiment is not capable of distinguishing between the production of radiation and the ionization of the gas.

A simple modification of Lenard's method, which enables this distinction to be made, was devised by Davis and Goucher, and has since been used by several experimenters. The modification consists in introducing another gauze *B* (Fig. 5) between the gauze *G* and the plate *P*, and in having a small difference of potential V_3 between *B* and *P*, in such a direction as to oppose positive ions travelling to *P*. If the distance between *B* and *P* is small, and if V_3 is about 1 volt, it will not prevent positive ions produced in the V_2 space from reaching the collecting electrode, but since it reverses the sign of *P*, making that electrode positive to the nearest gauze *B*, it reverses the photoelectric effect detected by the electrometer, for any radiation produced in the gas causes photoelectrons to leave *B* and to pass to *P*. Thus the electrometer gives a negative deflexion when radiation is produced in the gas and a positive deflexion when positive ions are collected.

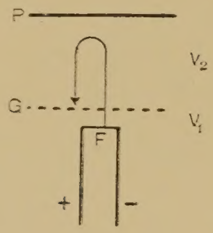


FIG. 4.

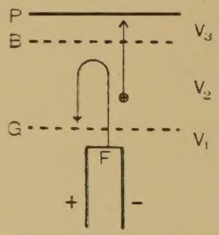


FIG. 5.

A very interesting method of detecting ionization has been devised by Hertz[*] which depends upon the influence which positive ions have in neutralising the space charge of negative electricity which limits the electron emission from a brightly glowing filament. This filament is represented by *H* in Fig. 6. It is maintained at a white heat, and the electron current from it to the surrounding electrode is measured by a galvanometer, the potential difference between *H* and *G* being small. The filament *F*, placed underneath and near to the gauze-covered opening *G*, is the source of the bombarding electrons whose energy is to be transferred to the gas

[*] *Loc. cit.*

atoms they collide with. At the very high temperature of the filament *H* the current from it is limited by the space charge of the "cloud" of electrons which surrounds it. As soon, however, as the electrons from *F* are able to ionize the gas in the apparatus, positive ions enter this cloud of electrons and neutralize its effect, thus causing an increase in the current measured by the galvanometer. This increase, therefore, marks the stage at which the energy of the bombarding electrons from *F* attains the ionization value.

THE SPECTROSCOPIC METHOD.

This method can be used for the measurement of the excitation potential of a gas or vapour if the radiation emitted when the displaced electron of the atomic system falls back into its normal orbit is in the visible or in the easily photographed part of the spectrum. As the energy of the electron stream is gradually raised, different critical potentials are reached, and new lines appear in the spectrum. When the ionization potential of the gas or vapour is attained, the arc spectrum may be seen or photographed. A form of apparatus which is very convenient for these experiments when gases are being experimented on is shown in Fig. 7, which is reproduced from a paper by Miss A. C. Davies.* The apparatus contains two parallel lime-coated platinum filaments *F*, *F*, (only one of which is used at a time) in order to avoid delay if a filament is fused. These filaments are fixed above the gauze cylinder *G* and the anode *A*, in a small glass vessel which is placed between the pole pieces *N* and *S* of an electromagnet. The energy of the bombarding electrons is controlled by the difference of potential applied between *F* and *G*. The electrodes *G* and *A* are usually maintained at the same potential and the space between these is viewed by the spectroscope. The magnetic field serves to concentrate the luminosity produced in the gas into a bright central column parallel to the slit of the spectroscope.

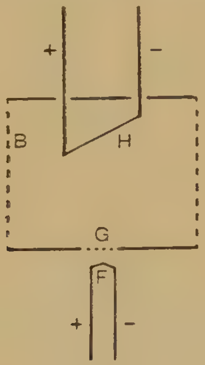


FIG. 6.

The spectroscopic method of experimenting cannot be used in all cases. For the permanent gases the radiation emitted at the excitation potential falls in the extreme ultra-violet part of the spectrum, and a vacuum grating spectroscope is necessary for its detection ; but even in these cases part of the arc spectrum, which appears at the ionization potential, falls within the limits of the visible region. However, for accurate observations of the voltage at which the arc spectrum is first produced it is necessary to have a large amount of ionization, and the method is thus not so sensitive as those in which a delicate electrometer can be used as the detecting instrument. But the spectroscope has one great advantage over the instruments which merely detect the presence of positive ions, for observations of the spectrum of the radiation produced remove all doubts as to the material which is being ionized. It has often happened that the ionization of some impurity present in the gas under test has been mistaken for ionization of the gas itself when electrical measurements only have been made.

---

* Proc. Roy. Soc., A., Vol. 100, p. 599 (1922).

A Brief Consideration of Some Results

It is only possible here to give a very brief reference to some of the results obtained by the experimental methods which have been described. The excitation and ionization potentials of certain of the elements of Group I of the Periodic Table have been investigated by Tate, Foote and Mohler, and for the elements Na, K, Rb and Cs, for which results have been obtained, one excitation potential and one ionization potential have been found for the vapour of each element. Moreover, the values of these critical potentials have been found to correspond to the first and the last terms respectively of a particular series of lines in the spectrum of the element—viz., that designated in the usual notation by $1\sigma - m\pi$. Thus, at the excitation potential of potassium vapour, a single spectrum line (or, more correctly, a single doublet) appears, and the frequency ν of this radiation is found to be connected with the excitation potential V by the relation $eV = h\nu$, where e is the elec-

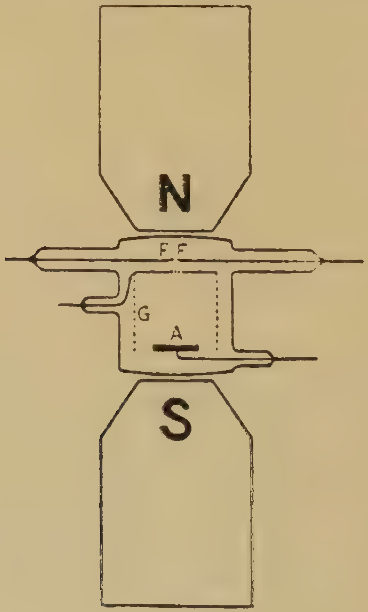


Fig. 7.

tronic charge and h is the constant known as Planck's constant. At the ionization potential of potassium vapour the complete arc spectrum is produced, and the highest convergence frequency of any series of the arc spectrum is found to be connected with the ionization potential by the same quantum relation given above. The observed values of the excitation and ionization potentials in the case of potassium are 1·55 volts and 4·1 volts respectively, whereas the values calculated by the quantum relation from the frequencies of the first and last lines of the series $1\sigma - m\pi$ are 1·61 volts and 4·32 volts respectively, values in very good agreement with those determined experimentally. If the energy of the bombarding electrons is raised considerably above the ionization value—e.g., to 25 or 30 volts—many more lines appear in the spectrum of the vapour. These are due to the bombardment removing (in some cases) more than one electron from the potassium atom. The new lines are produced when an electron falls into such a *multiply charged* potassium ion, and the atom is still positively charged while it is emitting this radiation. Recombination with the last electron (which renders the atom electrically neutral) produces lines of the arc spectrum only.* These results with potassium are typical of those obtained for the other alkali metals.

In the case of the metals of Group II of the Periodic Table, Foote and Mohler have found that two excitation potentials exist, and that these correspond to the first terms of two series of lines in the spectrum of the metal in question. For instance, in the case of magnesium, excitation potentials were found at 2·65 volts and at 4·42 volts, and ionization was found to begin at 7·75 volts. The spectroscopic investigation showed a single line only (corresponding to the excitation potential 2·65 volts) for voltages between 2·65 and 4·42 ; a two line spectrum (the lines corresponding to 2·65 volts and 4·42 volts) for voltages between 4·42 and the ionization value 7·61. For voltages slightly higher than this the full arc spectrum is produced, and for still higher voltages (e.g., 20 volts or 30 volts) the additional lines to be expected when multiple ionization of the atoms has occurred.†

It is important to notice that the evidence provided by these experiments on the elements of the first two groups of the Periodic Table indicates that on a collision taking place with sufficient energy an electron in the atom can be displaced from the normal orbit to the next outer orbit, or driven right out of the atom, but there is no evidence that it can be sent from the normal orbit to any intermediate orbit, for if such transitions occur there should be a definite excitation potential corresponding to each intermediate orbit. Two excitation potentials have been found for the elements of Group II, but these have been connected with the two distinct systems of series in the spectra of the Group II elements, which suggests the existence of two distinct sets of orbits in the atom, so that we can imagine the electron can get out of the atom in two different ways. The first excitation potential may be regarded as the voltage at which an electron is displaced to the first outer orbit of one system. The second excitation potential is the voltage at which an electron is displaced to the first outer orbit of the other system, and in neither case is there any evidence from these experiments that an electron can be displaced to any intermediate orbit by the collision of a bombarding electron.

---

* Slides of the various spectra of potassium vapour, from photographs given by Foote and Mohler were shown in the lecture.

† Slides of the various spectra of magnesium vapour, from photographs given by Foote and Mohler were shown in the lecture.

Evidence which appears to be in conflict with this is provided by Franck and Einsporn's results with mercury vapour.* These experimenters used a modification of Lenard's method, detecting the radiation produced by means of its photoelectric action, and increased the energy of their bombarding electron stream in very small steps. The curves reproduced in their paper show more than a dozen discontinuities between the first excitation potential and the ionization potential, which they claim correspond to critical energies at which the displacement of an electron in the mercury atom to an intermediate orbit occurs. In many cases they have connected the measured voltage with a known spectrum line, but there are several of the measured voltages which correspond to wave-lengths at present unknown in the mercury spectrum. It is very difficult to reconcile these results with the inelastic collision curves of Foote, Mohler and Meggers for mercury vapour, which indicate the occurrence of inelastic collisions at multiples, and sums of multiples, of the two excitation potentials only. It is also difficult to see why successive increases of photo-electric current should occur even if a different transition of an electron within the mercury atom does take place at each of the potentials indicated by the discontinuities in the curves. Further investigation is necessary to explain these points.

THE CASES OF THE SIMPLE ATOMS *H* AND *He*.

In the case of the elements in the two groups of the Periodic Table which have been referred to, the frequencies corresponding to the excitation and ionization potentials fall in an easily accessible region of the spectrum and information with regard to them can be obtained from a study of the absorption spectra of the elements, for it follows from Bohr's theory that the normal atom can only absorb radiations which correspond to transitions in the emitting atoms, resulting in the return of a displaced electron to its normal orbit. The absorption spectra of such elements may, therefore, be looked to for information with regard to the normal orbits, and thus to the structure of the atom in its normal condition. In the case of gases, however, none of the lines of the ordinary photographic spectrum are absorbed, for none of these lines result from transitions to the normal orbit, but arise from transitions between intermediate orbits. In such cases a knowledge of the excitation and ionization potentials is particularly valuable as evidence in regard to the normal state of the atom.

The investigation of the excitation and ionization potentials of hydrogen and helium is especially interesting because of the simple constitution of the atoms of these gases, for it is possible to calculate the values of the excitation and ionization potentials corresponding to any simple theory of the structure of the hydrogen or helium atom, so that the experimental results are a direct test of the theory. Bohr's view of the structure of the hydrogen atom has already been given. The generally accepted experimental value of the excitation potential, 10·2 volts, and of the ionization potential, 13·5 volts, are in accurate agreement with the values calculated by Bohr. Most of the experimenters, however, who have investigated the critical electron energies for hydrogen have had no means of deciding whether the critical points they have obtained have been due to *atomic* hydrogen or to the gas in its usual molecular condition. Some recently published researches† have shown

* Zeit. für Phys., 2, p. 18 (1920).

† P. S. Olmstead, Phys. Rev., 20, p. 613 (1922); O. S. Duffendack, Phys. Rev., 20, p. 665 (1922).

how to increase the proportion of electronic-atomic collisions occurring, by increasing the amount of dissociated hydrogen in the gas used, and have in this way justified the assumption that the experimental values quoted above refer to the atom. Evidence that these values are due to H and not to H_2 has also been obtained from a series of experiments recently carried out at the Royal Holloway College. These experiments have, in addition, thrown light on the processes occurring at the various critical potentials due to the molecule.

Bohr's original view of the structure of the helium atom was that the two electrons revolved at the opposite ends of a diameter in the same circular orbit about the positive nuclear charge $2e$, and he showed that the ionization potential of such a system should be 28·8 volts. Recent direct determinations have shown, however, that the ionization potential of helium is about 24·5 volts, and thus the ring configuration is not a correct representation of the structure of the normal atom. Now the arc spectrum of helium is peculiar in that it possesses two independent serial systems, namely (*a*) a series of single lines, and (*b*) a series of doublets, and in that no lines which are combination lines between the two systems have been observed. This latter fact suggested that the two serial systems of the helium arc spectrum have their origin in two different atomic configurations—indeed, on this account it was once thought that helium consisted of a mixture of two gases, to which the names orthohelium and parhelium were given.

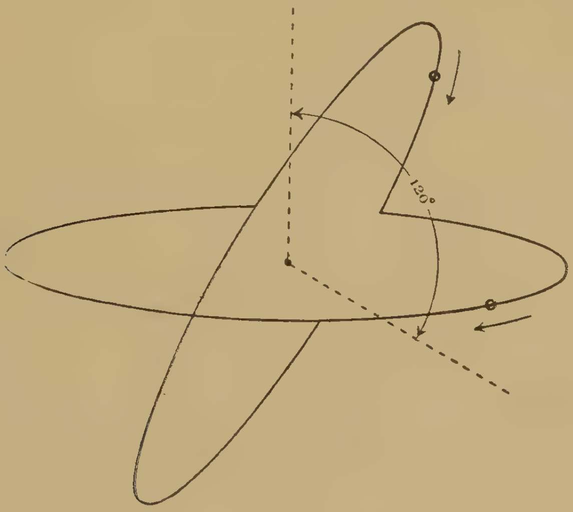


FIG. 8.

A model of the helium atom has recently been put forward by Bohr, according to which the two electrons of the helium atom revolve about the nucleus in two equivalent independent orbits, which are approximately circular, but are in planes inclined at an angle of 120 deg., as illustrated in Fig. 8. When one of these electrons has been removed from the atom, there are two possible sets of orbits which a recombining electron may take as it falls in towards the nucleus. One of these sets of orbits is coplanar with the orbit of the undisturbed electron, while the other set is inclined at an angle of 120 deg. with the orbit of that electron. These sets of orbits are known as the *coplanar* system and the *crossed* system respectively. Transitions of the outer electron between the various coplanar orbits give rise to spectrum lines of the doublet serial system, while transitions between the various orbits of the crossed configuration give rise to lines of the singlet serial system. In accordance with Bohr's theory, transitions between these two sets of orbits should not occur—a condition which we have seen is in agreement with the spectroscopic evidence.

It has been found experimentally that helium has two excitation potentials 0·8 volt apart and in the neighbourhood of 20 volts. The intervals between these excitation potentials and the ionization potential have been accurately measured, and found to be 4·8 volts and 4·0 volts respectively. Now 4·8 is the voltage which is connected by the quantum relation $eV=h\nu$, with the limiting frequency of the doublet principal series of helium, and 4·0 volts is the value connected by the same relation with the limiting frequency of the singlet principal series of helium. Thus 4·8 volts is the calculated potential difference through which an electron must fall in order to be able to remove an electron from the orbit which is concerned with the production of the principal series of doublets to a point right outside the atom. But at the ionizing potential an electron is removed from the *normal* orbit. Thus the lower (or first) excitation potential must correspond to the stage at which an electron is removed from the normal orbit to the first outer orbit connected with the doublet (or coplanar) system. By similar reasoning we see that at the higher excitation potential an electron is removed from the normal orbit to the first outer orbit connected with the singlet (or crossed) system. Since, according to the theory, transitions between the two systems of orbits do not occur, an electron falling into the atom by the coplanar set of orbits does not, if the theory is correct, fall into the normal orbit, because this belongs to the crossed system as illustrated in Fig. 8. It must therefore remain in the coplanar orbit of least energy. The atom in this condition is in a " metastable " state. It can only revert to the normal condition by the action of strong electric fields or by the agency of foreign atoms—e.g., atoms of gaseous impurities if any are present, or solid bodies such as the walls of the containing vessel, or the metallic electrodes in the apparatus. In the absence of gaseous impurities the atom will remain in the metastable condition until by diffusion it reaches these solid " impurities," when by some intermediate process (possibly in the nature of chemical combination) it attains once again its normal state without emitting radiation corresponding to the energy difference of the metastable and the normal conditions.

It must be observed that the reverse transition to that which we have just been considering—the transition which occurs at the first excitation potential—the removal of an electron from the normal orbit to the first outer orbit of the doublet system, is itself a transition, which, according to Bohr's theory, should not occur without external aid of the kind indicated, but it seems probable that the electric field due to the presence of the colliding electron in the near neighbourhood of the atom provides the perturbing force which makes the transition possible.

The view that the " life " of a helium atom in the abnormal condition resulting from an inelastic collision between a normal helium atom and an electron having the quantum of energy corresponding to the first excitation potential is of longer duration than that in other abnormal states, is supported by a certain amount of experimental evidence, but whether this state is metastable in the sense that the atom cannot revert directly from this state to the normal state with the emission of radiation is a matter on which the existing evidence is conflicting, and further experiments are necessary to elucidate the point.

IONIZATION BY CUMULATIVE EFFECTS.

It follows from Bohr's theory of atomic structure that the radiation which is emitted by an excited atom as it returns to the normal condition should be readily absorbed by another normal atom of the same element, so that, when this type of radiation is stimulated in a monatomic gas it should be passed on from atom to atom throughout the entire volume by this process of absorption and re-emission. That this process actually occurs is suggested by the production of ionization in a gas or vapour at a moderate pressure by the bombardment of electrons having energy in excess of that corresponding to the excitation potential, but less than that corresponding to the ionization potential. Ionization produced under these conditions cannot arise from the impact of a single electron, and the probability of its being due to the impacts of two or more electrons on the *same* atom may be shown to be very small. If, however, the radiation emitted by one atom can be absorbed by another atom, and so passed on throughout the whole volume of the gas, the probability of an encounter between a bombarding electron and an excited atom is very much increased, and at such an encounter ionization of the atom would, of course, be possible, if the energy of the impacting electron corresponded to a potential difference greater than the difference between the ionization potential and the excitation potential. In this way ionization of the gas below its normal ionization potential would be accounted for.

A direct proof that radiation produced at the excitation potential in a monatomic gas is passed from atom to atom in the manner indicated has been obtained by using an apparatus made in the form of a letter H, when it has been found that the radiation in such gases as argon and helium, if produced in one side tube, can pass round through the short horizontal tube, and produce a photo-electric effect on a screened electrode in the other side tube. This property of the radiation is an important factor in enabling an electric arc to be maintained in such gases at very low voltages.

The considerations which have been put forward illustrate the importance of an accurate knowledge of the excitation and ionization potentials of different elements as a direct experimental test of the correctness of various atomic models, particularly in those cases for which the easily photographed optical spectra are not associated with the normal condition of the atom in question.

I.—X-RAY ANALYSIS OF SOLID SOLUTIONS.

By E. A. Owen, *M.A.*, *D.Sc.*, and G. D. Preston, *B.A.*, The National Physical Laboratory.

Received May 30, 1923.

Abstract.

(1) The atomic structure of solid solutions of copper-aluminium, aluminium-magnesium, and copper-nickel has been examined by the X-ray spectrometer. In each case it was found that the solute atom replaces an atom in the lattice of the solvent, the substitution being accompanied by a distortion of the lattice.

A saturated solution of aluminium in copper shows that the aluminium expands the copper lattice from 3·60Å to 3·65Å. The effect of adding nickel to copper was to produce a contraction of the lattice, the contraction being approximately a linear function of the atomic percentage of either constituent. The addition of 8 per cent. magnesium by weight to aluminium causes the average parameter of the aluminium lattice to increase from 4·05Å to 4·10Å. The addition of 8 per cent. aluminium by weight to magnesium decreases the average parameter of the hexagonal lattice of magnesium from 3·17Å to 3·15Å, and increases its axial ratio from 1·63 to 1·66.

(2) An examination of the eutectic alloy of aluminium and copper showed that this alloy consists of a mixture of two distinct substances with different space lattices. The one substance being $CuAl_2$ and the other a substance, the space lattice of which could not be distinguished from that of pure aluminium.

(3) The intermetallic compound $CuAl_2$ was found to possess a simple tetragonal lattice of side 4·28Å and axial ratio 0·562, the copper atoms being at the corners and the aluminium atoms at the centres of the four small faces.

(4) The atomic structure of the compound Cu Al resembles that of a solid solution of aluminium in copper, but the distortion is considerably greater. The material was found to have a face centred trigonal lattice of side 3·89Å and an angle between the axes of 94·6°, the 111 planes being composed alternately of aluminium and copper atoms.

I. Introductory.

In an attempt to explain the hardness of solid solutions from the consideration of crystal structure, Rosenhain[*] advanced the view that crystals of solid solution of metal *B* in metal *A* are built on the same space lattice as crystals of pure *A*, the sole difference being that a certain number of individual atoms of *A* are replaced by atoms of *B*. The substitution of *B* atoms for *A* atoms is accompanied by a slight distortion of the *A* lattice in the neighbourhood of the *B* atoms, the extent of the distortion depending upon the relative sizes of the two atoms.

There is another way in which atoms of *B* may enter into the *A* lattice. Instead of replacing an atom of the solvent *A*, the solute atom may take up its position in the interstices between the atoms of the *A* lattice. There is experimental evidence to show that both of these arrangements actually occur.

Bain,[†] in an extensive investigation which included the examination of a number of different series of solid solutions, arrived at the conclusion that the arrangement of the atoms was in each case similar to that assumed by Rosenhain. The alloys examined were solutions of tin, zinc, manganese or aluminium in copper; iron or zinc in silver; tungsten, molybdenum, chromium or managanese in iron. McKeehan* found that in the silver-palladium and the silver-gold series of alloys the atoms in the crystals of both the pure metals and the alloys are arranged on face centred lattices, and that in the silver-palladium series in particular the parameter is nearly a linear function of the atomic per cent. of either component.

---

[*] Rosenhain, Proc. Roy. Soc., A., Vol. 99, p. 196 (1921).

[†] Bain, Chem. & Met. Eng., Oct. 5, p. 663 (1921); Jan. 3, p. 21 (1923); Jan. 10, p. 65 (1923).

The work of Westgren and Phragmen† on the crystal structure of steel points to the conclusion that the carbon atoms are located in the interstices of the iron lattice.

In all the above investigations the photographic X-ray method of analysis was employed. The present Paper gives an account of a series of experiments on different alloy systems carried out with the Bragg X-ray spectrometer, the intensity of the reflections being measured by means of an ionisation chamber. The object of the experiments was to obtain further data regarding the structure of solid solutions, and to attempt, if possible, to increase the accuracy of measurement with a view to differentiating the more easily between what may be termed the "substitutional" and the "interstitial" atomic arrangements.

From a knowledge of the specific volume of a solid solution, together with the data obtained from X-ray analysis, it is possible to distinguish between these two types of solution. The argument is based upon the assumption that the introduction of a solute atom into the space lattice of a metal distorts the lattice, and that the X-ray spectrometer measures the average spacing between successive layers (no longer planes) of atoms. If we are dealing with a face-centred cubic lattice, then the side of the cube a, the density ρ, and the atomic mass M associated with each point of the lattice are connected by the relation

$$\frac{4M}{a^3}=\rho. \qquad \qquad (1)$$

If the solution is of the substitutional type and there are N_2 atoms of a metal of atomic weight M_2 dissolved in N_1 atoms of a metal of atomic weight M_1, then the average mass associated with each point of the lattice will be

$$M_s=M_1+\frac{N_2}{N_1+N_2}\cdot(M_2-M_1). \qquad \qquad (2)$$

On the other hand, if the solution is interstitial, there will be associated with each point a mass

$$M_i=M_1+\frac{N_2}{N_1}\cdot M_2. \qquad \qquad (3)$$

Provided there is a sufficient atomic percentage of dissolved material, it is possible by the X-ray spectrometer to detect and measure the change in the parameter of the space lattice of the solvent metal. A comparison of the observed value of the parameter with the values calculated from the observed density on the substitutional and interstitial theories suffices to decide in the cases investigated, with one exception, between these two possible atomic arrangements.

---

* McKeehan, Phys. Rev., Vol. 20., p. 424, Nov. (1922).

† Westgren and Phragmen, Journ. Iron & Steel Inst., Vol. 105, p. 241 (1922).

II. EXPERIMENT.

The method of procedure has been described by the authors* in a previous Paper. A plate of metal to be examined, about 2 cm. wide, polished and etched, and containing throughout its volume small crystals (the smaller the size of the individual crystals the better for the purpose of the experiment) is placed on the table of the X-ray spectrometer. A beam of radiation from a molybdenum anticathode is allowed to fall on this plate, and the intensity of the "reflected" beam is measured in the usual way. To arrive at the correct angles of reflection, two corrections have to be applied to the observed readings on account of (1) the flatness of the plate, and (2) the penetration and the consequent absorption of the radiation in the plate. It is desirable to consider these two corrections in detail.

(1) *Correction for Flatness of Specimen.*

The conditions of reflection of a beam of X-rays diverging from a point S (Fig. 1) are such that if there are situated at points A, M, B, concyclic with S, suitably orientated crystals, the reflected rays will converge to a focus at S' on the circle $SAMB$. If a flat plate is used, then evidently the ray SA striking it at A' will be reflected along $A'Q$ parallel to AS', so that the energy from the point S is spread out over the region QS'. As the slit of the ionisation chamber is moved across this region, a maximum intensity will be recorded when the edges of the slit coincide with Q and S', so that to obtain the proper angle of reflection we will have to add to the observed angle one-half of the angle QMS'.

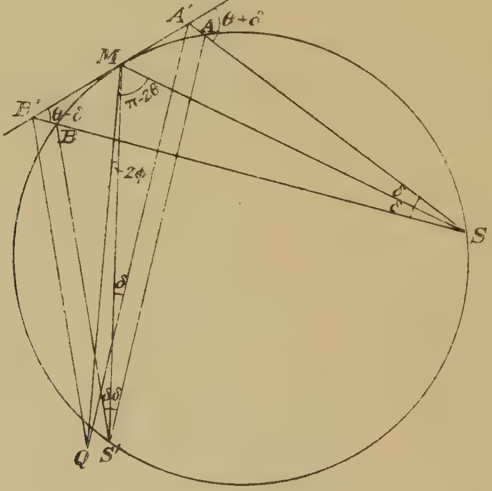


FIG. 1.

---

* Owen and Preston, Proc. Phys. Soc., Vol. 35, p. 101, Feb. (1923).

If 2δ is the angular divergence of the beam of X-rays and if $l=SM$, then

$$A'M=l\delta/\sin(\theta+\delta) \text{ and } B'M=l\delta/\sin(\theta-\delta),$$

and from the triangles $A'QM$ and $B'QM$

$$\frac{\sin A'QM}{l\delta/\sin(\theta+\delta)}=\frac{\sin QA'M}{QM} \text{ and } \frac{\sin B'QM}{l\delta/\sin(\theta-\delta)}=\frac{\sin QB'M}{QM},$$

or, since $QA'M=\theta-\delta$ and $QB'M=\pi-\theta-\delta$

$$\sin A'QM=\frac{l\delta\sin(\theta-\delta)}{QM\sin(\theta+\delta)} \text{ and } \sin B'QM=\frac{l\delta\sin(\theta+\delta)}{QM\sin(\theta-\delta)}. \quad . \quad . \quad . \quad (4)$$

From the parallelism of AS', $A'Q$, and BS', $B'Q$

$$A'QM+B'QM=2\delta$$

Provided $A'QM$ and $B'QM$ are small, which in practice is the case, from (4) we have

$$\frac{A'QM}{B'QM}=\frac{\sin^2(\theta-\delta)}{\sin^2(\theta+\delta)}$$

whence

$$A'QM=\frac{2\delta\sin^2(\theta-\delta)}{\sin^2(\theta+\delta)+\sin^2(\theta-\delta)}$$

Referring to the figure, the lines $A'Q$ and MS' intersect at an angle equal to δ, so

$$QMS'=2\varphi=\delta-A'QM$$

or

$$\varphi=\frac{\delta}{2}\cdot\left(\frac{\sin^2(\theta+\delta)-\sin^2(\theta-\delta)}{\sin^2(\theta+\delta)+\sin^2(\theta-\delta)}\right).$$

For small values of θ the length of the specimen $A'B'$ may be insufficient to obstruct the whole beam of divergence 2δ. When this is the case the quantity $\delta'=\frac{A'B'\sin\theta}{2l}$ must be substituted for δ in computing the value of φ, whenever δ' is less than δ. Thus, for the instrument used in the present work when the bulb slit is set at 2 mm. $\delta=34'$ and consequently for a specimen 2 cm. wide, l being 15 cm., for values of θ up to 8 deg. (when δ' becomes approximately equal to δ) the expression given for δ' is substituted for δ. The following table shows the values of φ computed from the above expression for a few values of θ for a specimen 2 cm. in width :—

TABLE I.

θ	φ
5°	2·5′
8°	2·5′
10°	2·0′
15°	1·2′

(2) *Correction for Depth of Penetration.*

Suppose AB (Fig. 2) to be the surface of the specimen and S a point in the bulb slit—then the rays diverging from S and reflected by crystals lying in the circle AMB will converge to a focus at S'. The distance traversed in the metal by a ray such as SNS' varies from zero at A and B to $2ML/\sin\theta$, so as an approximation we may suppose that the average value of this quantity for all the rays diverging from S is $ML/\sin\theta$. If now we further suppose that the intensity at S' is proportional to the length AMB, we can find the value of ML for which the intensity is a maximum.

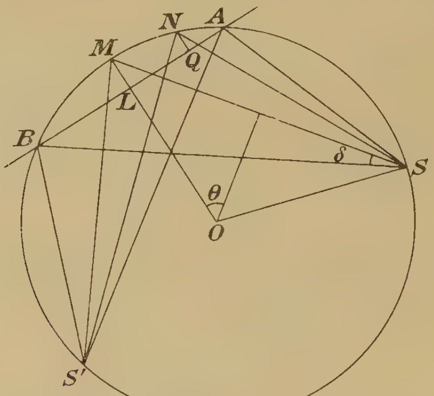


FIG. 2.

Writing $ML=x$, $SM=l$; $OS=R$ and $\angle ASM=\delta$, we have

$$AM=2R\delta=\frac{l\delta}{\sin\theta}$$

Subject to the above assumption, the intensity at S' is

$$I=Ke^{-\frac{\mu x}{\sin\theta}}\cdot\frac{2l\delta}{\sin\theta}.$$

Moreover $$\delta=\sqrt{\frac{x}{2R}}\text{ approximately,}$$

so that $$I=Ke^{\frac{\mu x}{\sin\theta}}\cdot\frac{2l}{\sin\theta}\cdot\sqrt{\frac{x}{2R}}.$$

Differentiating with respect to x and equating to zero, we have

$$x=\frac{\sin\theta}{2\mu}.$$

This gives the value of ML for which the intensity is a maximum. The require correction is the angle subtended by ML at S', i.e.,

$$\varphi'=\frac{ML\ .\cos\theta}{l}=\frac{\sin 2\theta}{4\mu l}.$$

In the case of aluminium, μ is 13 for K_α radiation of molybdenum, so that with the instrument previously referred to where l=15 cm. the value of φ' is about 4 minutes of arc when θ=45 deg. When θ is 10 deg., φ'=1·5 minutes. For the heavier metals such as copper, nickel, iron, the correction is very much less than the experimental error as μ increases rapidly with atomic weight.

Both of the above corrections are small over the range of angles employed in the present investigation, but they have been applied to the observations tabulated below.

III. RESULTS.

(1) *Aluminium Copper Alloys.*

(*a*) *Alloys Rich in Copper.*—A series of solid solutions of aluminium in copper, containing 2, 4, 6 and 8 per cent. of aluminium by weight, was examined. It was found that there was a general shift of the lines in the observed spectra towards the origin, showing that the lattice is expanded by the presence of the aluminium atoms (Fig. 3). The form of the lattice, however, was still that of the face centred cube characteristic of copper. The reflection of the K_α radiation of molybdenum

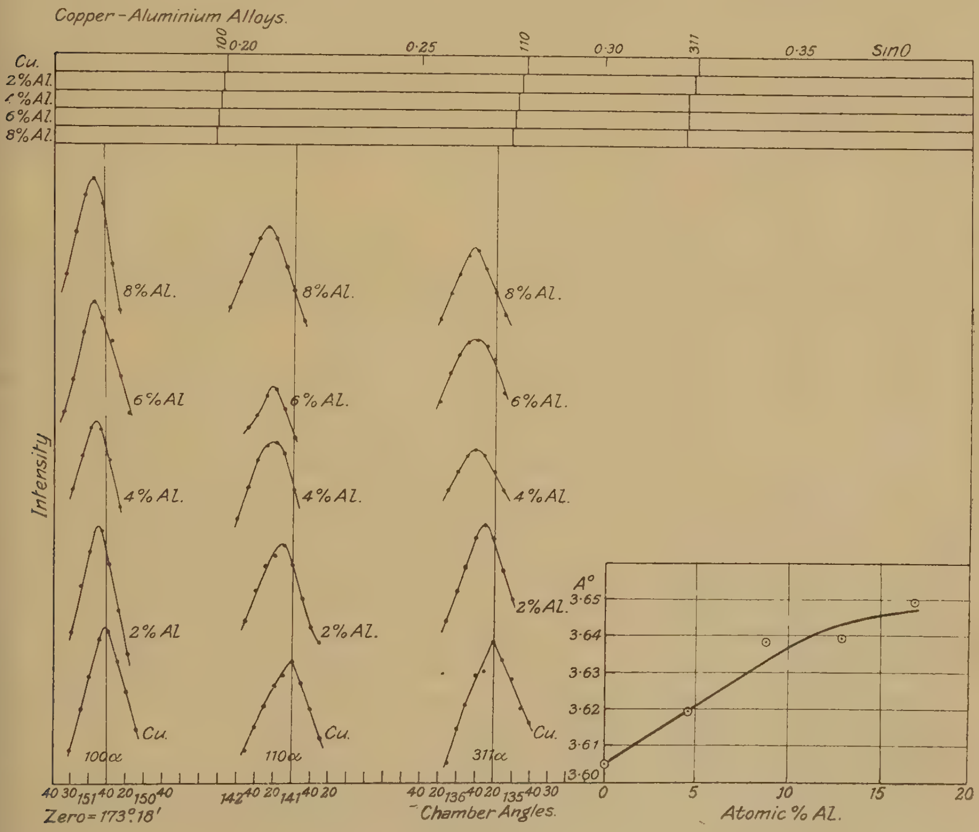


FIG. 3.

from the 110 and 311 planes was examined in detail, the maximum being fixed to within 3′ of arc for the whole series. The angles of reflection and the values of the corresponding parameters of the lattices are given in Table II.

Table II.

Form.	Copper.		2% Al.		4% Al.		6% Al.		8% Al.	
	θ	a	θ	a	θ	a	θ	a	θ	a
110…………	16° 9′	3·599	16° 4′	3·617	16° 0′	3·633	15° 58′	3·635	15° 54′	3·653
311…………	18° 58′	3·612	18° 55′	3·621	18° 48′	3·642	18° 48′	3·642	18° 47′	3·646
Mean Value		3·605Å		3·619Å		3·638Å		3·639		3·649Å

The lattice constant increases from 3·60Å for copper to 3·65Å for the alloy containing 8 per cent. aluminium.

In Table III. the values of the densities of the alloys are compared with values calculated on the assumption that the aluminium atom replaces a copper atom on the distorted lattice, the side of the cube found by the X-ray analysis being supposed to be the average spacing in the material.

Table III.

%Al.	$\frac{4M_s}{a^3}$ grms. per c.c.	ρ obsd.	Diff.	$\sqrt[3]{\frac{4M_s}{\rho}}$	a obsd.	Diff.
0	8·96	8·93	+·03	3·608Å	3·605Å	—·003
2	8·63	8·63	±·00	3·618	3·619	+·001
4	8·27	8·33	—·06	3·629	3·638	+·009
6	8·06	8·04	+·02	3·642	3·639	—·003
8	7·80	7·74	+·06	3·659	3·649	—·010

The appropriate value of M_s, the average atomic weight, was calculated by the aid of Equation (2) for each specimen. The differences between the observed and calculated values of ρ are not greater than 0·8 per cent., which, in view of the fact that the experimental error has been cubed, is very fair agreement. The alternative of supposing the aluminium atom to be situated in the interstices of a distorted copper lattice gives too high a value for the density. If the calculation were based on the observed value of the density, a lattice the average parameter of which is 3·89Å would be required in the case of 8 per cent. aluminium alloy. The fact that we find in this case a lattice, the parameter of which is 3·65Å, and that the calculated density is in good agreement with the observed density would indicate that the solution is of the substitutional type.

(*b*) *Alloys Rich in Aluminium.*—No shift of the spectrum could be detected in specimens of aluminium-copper alloy containing 0·5, 1·0, 1·5, 2·0, 3 and 4 per cent. copper respectively. The aluminium lattice persists throughout the series the amount of distortion, if any, being within the limits of experimental error. In the 0·5 per cent. specimen some lines are unaccounted for at the small angle end of the spectrum and in the 1 and 1·5 per cent. alloys 311 appears to be a doublet.

The reflections of K_α radiation of molybdenum from the 110 and 311 planes were observed in detail for the first four of the series. The results are given in

Table IV. The figures show that there is no change of the lattice constant within the error of experiment. Neither is it possible in this case to distinguish between the substitutional and the interstitial arrangement of the atoms from a comparison of the densities.

TABLE IV.

Form.	Aluminium.		0·5% Cu.		1·0% Cu.		1·5% Cu.		2·0% Cu.	
	θ	a	θ	a	θ	a	θ	a	θ	a
110............	14° 21′	4·039	14° 23′	4·029	14° 21′	4·039	14° 19′	4·048	14° 21′	4·039
311............	16° 53′	4·042	16° 53′	4·042	16° 55′	4·033	16° 51′	4·051	16° 54′	4·038
Mean Value		4·040		4·036		4·036Å		4·050Å		4·039Å

(c) *Aluminium-Copper Alloy containing* 30 *per cent. Copper by Weight.*—An alloy containing 70 per cent. aluminium and 30 per cent. copper by weight is of interest, as its composition is nearly that of the eutectic alloy. An examination of a small plate of this material by the X-ray spectrometer gave a spectrum containing 18 lines, the sines of the observed angles of reflection being given under the heading AC_{30} in Table V. For the sake of comparison the lines of aluminium and those of the compound Cu Al_2, the structure of which is described below, are also included. The lines in the observed spectrum of AC_{30} may be divided into two groups—the one group containing aluminium lines and the other group containing Cu Al_2 lines. The eutectic alloy would thus appear to consist of a mixture of aluminium and the intermetallic compound Cu Al_2. In the preceding section it was concluded that with the accuracy so far attained with the present method of analysis it is impossible to distinguish between pure aluminium and a saturated

TABLE V.

Aluminium.		AC_{30}	Cu Al_2	
Form.	Sin θ	Sin θ	Sin θ	Form.
...	...	...	0·074	100β
...	...	...	0·083	100α
...	...	0·100	0·104	110β
...	...	0·118	0·117	110α
111β	0·131	0·132	...	...
111α	0·152	0·150	0·148	001α
...	...	0·166	0·165	200α
100α	0·175	0·176	...	...
...	...	0·187	0·185	210α
110β	0·221	0·218	...	...
110α	0·248	0·246	...	...
311β	0·259	0·257	...	...
...	...	0·276	0·279	301α
311α	0·290	0·291	0·293	002α
...	...	0·299	0·301	320α
222α	0·307	0·311	...	...
...	...	0·332	0·334	400α
...	...	0·347	0·343	330α
331α	0·385	0·385	...	...
210α	0·395	0·393	...	...

solid solution of copper in aluminium. The limit of solid solubility being in the neighbourhood of 1 atomic per cent. of copper the distortion of the aluminium lattice is too small to be detected with certainty. Thus, although the lines in the spectrum of AC_{30} which are not attributable to $CuAl_2$ appear to be due to a lattice identical with that of pure aluminium, they may be due to a saturated solid solution of copper in aluminium. A metallurgical study of the alloy shows that this is actually the case. The definite conclusion arrived at from the present analysis is that the eutectic alloy consists of a mixture of two distinct substances arranged on different space lattices, the one substance being $CuAl_2$ and the other a substance whose space lattice cannot be distinguished from that of pure aluminium.

(*d*) *Structure of* $CuAl_2$.—The results given in Table VI. were obtained with a cast flat plate of material containing the proper proportion of copper and aluminium. The observed lines agree approximately with a close-packed hexagonal structure, the side of the hexagon being 4·95 Å and the axial ratio 0·866. This structure had to be rejected because the first and second order reflections from the $11\bar{2}0$ planes and the third order from $10\bar{1}0$, which should be present, were missing. An alternative structure was found to be provided by a simple tetragonal lattice

TABLE VI.
$CuAl_2$.

Intensity.	2 θ	Sin θ	Form.	d	a (c=0·562)
1·1	8·5	0·0741	100β	a	4·25Å
4·0	9·5	0·0828	100α	a	4·27
0·9	12·0	0·1045	110β	$a/\sqrt{2}$	4·26
3·2	13·4	0·1167	110α	$a/\sqrt{2}$	4·29
1·0*	16·9*	0·1478	001α	ac	4·26
1·2	17·1	0·1487	200β	$a/2$	4·24
5·3	19·0	0·1650	200α	$a/2$	4·29
7·5	21·3	0·1849	210α	$a/\sqrt{5}$	4·29
2·6	26·9	0·2325	220α	$a/2\sqrt{2}$	4·30
...	30·2*	0·2605	002β	$ac/2$	4·30
3·3	30·5	0·2630	310α	$a/\sqrt{10}$	4·26
15·0*	34·1*	0·2932	002α	$ac/2$	4·29
1·8	35·0	0·3007	320α	$a/\sqrt{13}$	4·24
0·5	39·0	0·3338	400α	$a/4$	4·24
2·1	40·1	0·3428	202α	$a/3\sqrt{2}$	4·22
...	43·5	0·3705	420α	$a/2\sqrt{5}$	4·27
...	49·3	0·4171	440β	$a/4\sqrt{2}$	4·27
0·01*	52·7*	0·4439	003α	$ac/3$	4·26
...	62·7*	0·5202	004β	$ac/4$	4·31
2·0*	71·6*	0·5850	004α	$ac/4$	4·31
...	19° 0′	0·1650	200α	$a/2$	4·29
...	19° 18′	0·1677	101α	$a/\sqrt{1+\frac{1}{c^2}}$	4·31
...	21° 22′	0·1840	210α	$a/\sqrt{5}$	4·30
...	21° 38′	0·1877	111α	$a/\sqrt{2+\frac{1}{c^2}}$	4·29

of side 4·28 Å and axial ratio 0·562 (*see* Fig. 4). The intensities of the reflections from the 001 planes were so small, however, that it was considered desirable to examine the reflections from these planes more in detail. We were able to do this by the use of a number of single crystals of $CuAl_2$ in the form of rods about 3 mm. diameter and 3 or 4 cm. in length which Dr. Hanson, of the Metallurgical Department, kindly prepared for us. These were cut perpendicular to their length and mounted together so as to provide a surface about 1 cm. square for examination. In this way we were able to detect with certainty the first four orders of reflection from the 001 planes; the angles marked with asterisks in the first column of Table VI. were obtained with this specimen. The relative intensities of the observed spectra were as follows : —

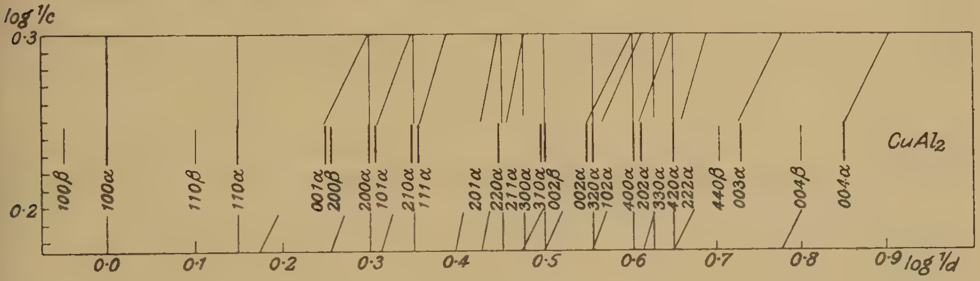


FIG. 4.

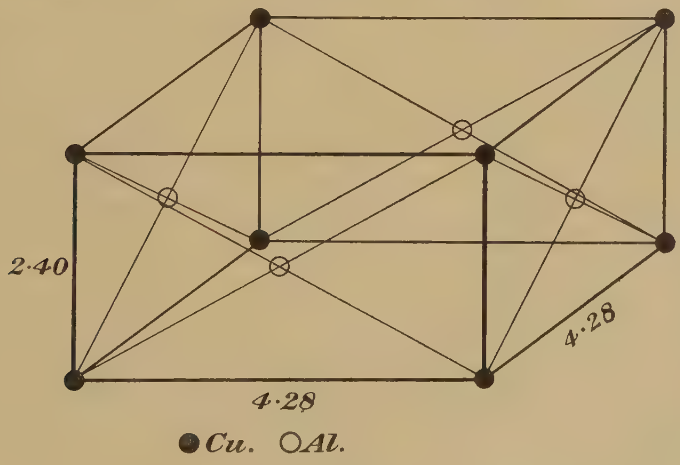


FIG. 5.

$$I_1 : I_2 : I_3 : I_4 : = 7 : 100 : 0{\cdot}7 ; \quad 14$$

These agree tolerably well with the calculated intensities, viz., 2·2 : 100 : 0·2 : 10 on the assumption that planes of copper and aluminium occur alternately. The spacing of the 001 planes calculated from the above observations gave the value 2·40 Å. A tetragonal structure of sides 4·28 Å and 2·40 Å having a copper atom at each corner and an aluminium atom at the centre of each of the four small faces is found to account satisfactorily for the observed intensities. A unit cell of the material is shown in Fig. 5. In this arrangement the 100 planes are alternately composed of Cu Al and Al. The first and third orders will accordingly be weak, the second and fourth strong. The spectrum curve showed this to be the case. A similar agreement between theory and experiment was obtained for other planes in the crystal. Further, the molecular weight of the compound is 117·77 and the density is 4·36, so that the number of molecules associated with each cell is :—

$$n=\frac{\rho a^3 c}{M}=0\cdot988$$

which is, within experimental error, in accordance with the value unity required by the above structure.

(*e*) *Structure of Cu Al.*—A small specimen of material, containing equal atomic percentages of copper and aluminium, was investigated. The intensities of the reflections were small, but by repetition it was found possible to arrive at the figures given in Table VII. The lines in the spectrum were found to fit on a plot representing a face centred trigonal structure with the axes inclined at an angle of 94·6 deg.

TABLE VII.
Cu Al.

$2\ \theta$	Sin θ	Form.	d	a
9·4	0·0819	...	...	...
15·8	0·1374	$\bar{1}11\beta$	0·5907 × a	3·88Å
17·8	0·1547	$\bar{1}11\alpha$	0·5907	3·88
19·8	0·1719	111α	0·5290	3·89
21·3	0·1849	100α	0·4965	3·86
25·2	0·2181	$\bar{1}10\beta$	0·3675	3·92
28·6	0·2470	$\bar{1}10\alpha$	0·3675	3·90
31·5	0·2714	110α	0·3367	3·88
33·8	0·2907	$\bar{3}11\alpha$	0·3120	3·90
35·3	0·3032	$3\bar{1}1\alpha$	0·3018	3·87
35·9	0·3082	$\bar{2}22\alpha$	0·2953	3·88
42·7	0·3641	200α	0·2483	3·91
			Mean $a=$	3·89Å

$$\eta=94\cdot6^\circ$$

$$2d_{100}=3\cdot86\,\text{Å}$$

$$M=90\cdot67\times\frac{1\cdot663}{1.008}\times10^{-24}\text{ grammes.}$$

$$\rho=\frac{M}{a^2 d_{100}\sin\eta}=5\cdot13\text{ gms. per c.c.}\ ;\quad \rho\text{ (observed)}=5\cdot25\text{ gms./c.c.}.$$

As will be seen from the table, the calculated values of "*a*," the side of the rhomb, do not differ from their mean value by as much as 1 per cent. The average value of the side of the rhomb is 3·89Å, which corresponds to a density of 5·13 gms. per c.c., on the assumption that there are two molecules of Cu Al associated with each face centred unit rhomb. The observed value of the density is 5·25 gms. per c.c., which would require a lattice of side 3·86 Å. The intensities of the reflections are too small to justify deductions as to the position of the atoms on the lattice, but if the occurrence of a line at 9·4° may be taken as indicating the presence of a spacing double that of the 111 spacing of this arrangement, then it suggests that the 111 planes are alternately composed of copper and aluminium atoms. The 100 and $\bar{1}11$ planes would then be composed of equal numbers of copper and aluminium atoms and no "half" order reflections would be expected. The structure could be produced from the lattice of aluminium by a contraction from 4·05 to 3·89 Å and a distortion of the cubic axes until they are inclined at 94·6°, or from the copper lattice by the same angular distortion of the axes accompanied by an extension from 3·60 to 3·89 Å in the side of the cell. The average distortion produced by the substitution of an aluminium atom for a copper atom on the copper lattice has been given in another section of this Paper. It was there found that the value of the parameter of the lattice reaches a maximum of 3·65 Å with about 12 atomic per cent. of dissolved aluminium. The structure of Cu Al suggested here bears a very close resemblance to the type of solid solution suggested by Tammann* and referred to by Bain.† The distortion of the lattice in this case is however more marked than in the cases cited for example by Bain in which atomic ratios of 3 to 1 are considered.

(2) *Alloys of Aluminium and Magnesium.*

An alloy containing 8 per cent. magnesium by weight gave a spectrum which was similar to that of aluminium, i.e., a face-centred cube, but the lattice showed a small expansion. A series of measurements were made of the lines reflected from the 111, 100, 110 and 311 planes (Fig. 6). The results are shown in Table VIII. In Fig. 6 the position of the aluminium lines is shown on the same graph as those observed in the present case.

TABLE VIII.

Form.	θ	Sin θ	a
111β	7° 35′	0·1319	4·129 Å
111α	8° 33	0·1487	4·121
100α	10° 0	0·1736	4·078
110α	14° 7	0·2439	4·104
311α	16° 39	0·2865	4·097

The value of "*a*" may be taken as 4·106 Å cm. with a possible error of 0·5 per cent. The density of the alloy is 2·57 gms. per c.c. and, on the substitution theory of solid solution, this gives a value 4·10 Å cm. for the average spacing of the lattice. Interstitial solution would require a spacing of 4·23 Å cm. to give the observed density, or a density of 2·81 gms. per c.c. to give the observed value of the lattice.

We may conclude, therefore, that the magnesium atoms replace aluminium atoms on the space lattice, producing a distortion of the lattice from 4·05 to 4·10 Å.

A second alloy of aluminium and magnesium containing 92 per cent. by weight of magnesium was found to possess a spectrum similar to that of magnesium, characteristic of a close packed hexagonal lattice. In order to ascertain which of the two constants, the side a of the hexagon or the axial ratio c, was affected by the introduction of the aluminium atom, careful measurements were made of the reflections from the $10\bar{1}0$, 0001, $\bar{1}011$ and $20\bar{2}2$ planes of the material (Fig. 7). The reflections from these planes were very sharp. They are shown graphically in Fig. 7. The observed angles of reflection are given in Table IX., together with the values of these angles after the correction for penetration has been made. The values of the

---

* G. Tammann, Zs. f. Anorg. u. Allgem. Chem., 107, pp. 1—239 (1919).

† *Loc. cit.*

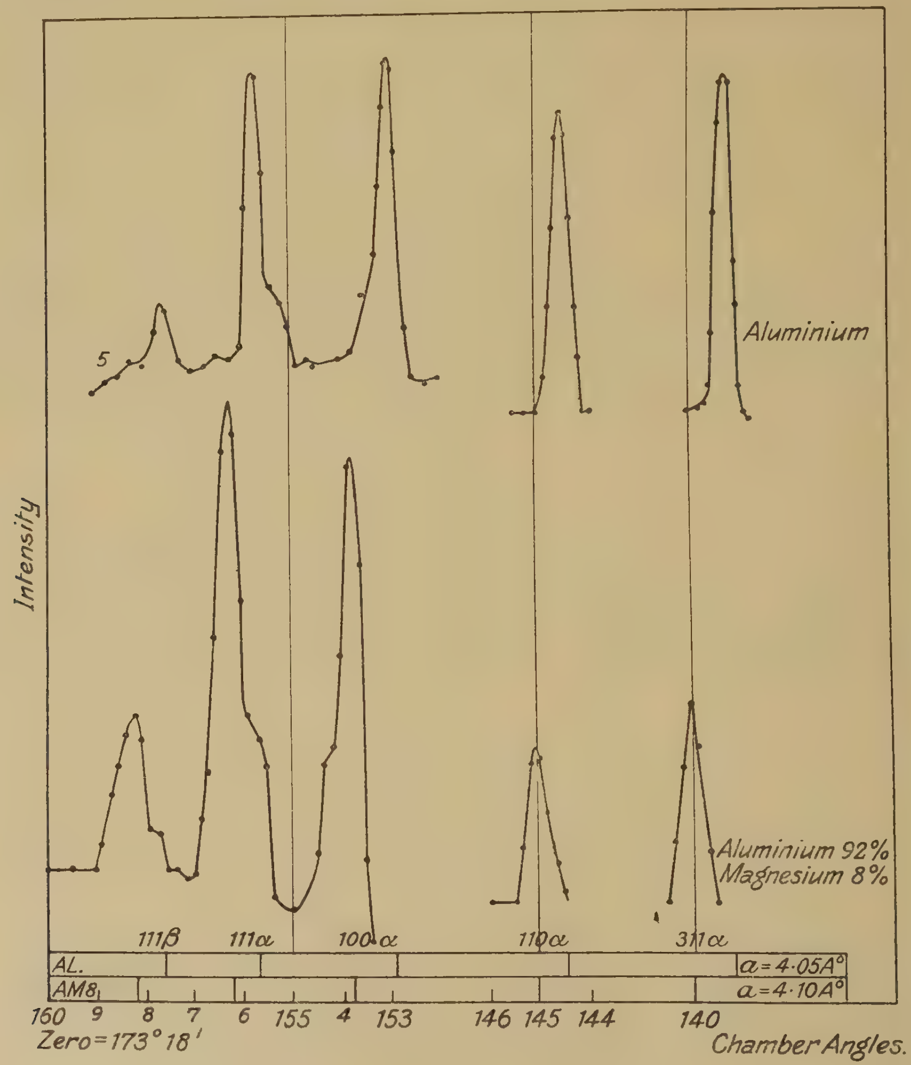


FIG. 6.

experimental error given are the maximum possible and the probable error in the value of sin θ is not more than 0·2 per cent. in each case.

TABLE IX.

AM_{91}

θ_1 observed.	θ_2 corrected.	Sin θ_2	d	Form.
7°24′±1′	7°27′	0·1297±0·0003	$\frac{a\sqrt{3}}{2}$	$10\bar{1}0$
7°45′±1′	7°48′	0·1357±0·0003	$\frac{ac}{2}$	0001
8°22′±1′	8°25′	0·1464±0·0003	$a/\sqrt{\frac{4}{3}+\frac{1}{c^2}}$	$10\bar{1}1$
16°57′±2′	17°0′	0·2924±0·0006	$a/2\sqrt{\frac{4}{3}+\frac{1}{c^2}}$	$20\bar{2}2$

$$a=3{\cdot}151\,\text{Å}$$

$$c=1{\cdot}660$$

$$\rho\ (\text{calcd.})=1{\cdot}80 \text{ grammes per c.c.}$$

$$\rho\ (\text{observed})=1{\cdot}79 \text{ grammes per c.c.}$$

The specimen may be taken to have been correctly centred on the instrument, since the value of the sin θ for $10\bar{1}1$ differs by less than 0·2 per cent. from the value of sin θ for $20\bar{2}2$. From the observation on $10\bar{1}0$, the value of "a" is calculated directly and gives the result 3·151±0·007 Å. Using this value of "a" and taking $\sin\theta_{10\bar{1}1}=0{\cdot}1463$ (the mean of the values obtained from the first and second order spectra), the value of "c" is found to be 1·660±0·007. As a check on these figures, we have the value of $d_{0001}=\frac{ac}{2}=2{\cdot}614$ in good agreement with the observed value $d_{0001}=\frac{\lambda_a}{2\sin\theta_{0001}}=2{\cdot}608$, where $\lambda_a=0{\cdot}70783$ Å.

For pure magnesium $a=3{\cdot}17$ Å and $c=1{\cdot}63$, so that the introduction of the aluminium atom into the magnesium lattice produces a slight contraction of the side of the hexagon, but increases the average distance between the successive hexagonal planes

The observed density of the specimen is 1·79 gms. per cubic centimetre. Calculating the density on the assumption that the aluminium atom replaces a magnesium atom on the lattice, the figure 1·80 is obtained. If the aluminium atom were accommodated in the interstices of the lattice, a density of 1·94 would be required to account for the observed spacings, alternatively to account for the observed density, with $a=3{\cdot}151$ Å, interstitial solution would reqiure the axial ratio to be equal to 1·81, while the substitutional hypothesis yields the figure 1·68 in agreement with observation. There appears therefore to be no doubt that the aluminium atom nters into solution by replacing a magnesium atom, the side of the hexagon being decreased from 3·17 to 3·15 Å, and the distance between successive hexagonal layers being increased from 5·17 to 5·23Å.

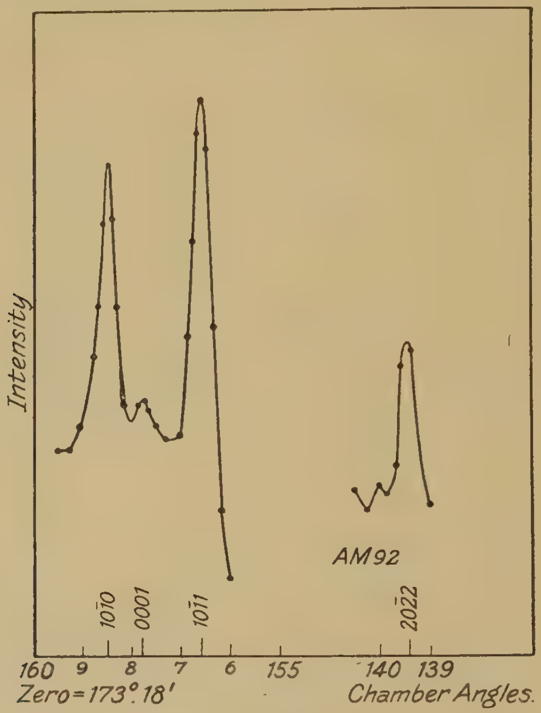


FIG. 7.

(3) *Copper-Nickel Alloys.*

The results obtained with alloys of copper containing 10, 20, 30 and 40 per cent. of nickel by weight are included in Table X. It will be observed that the

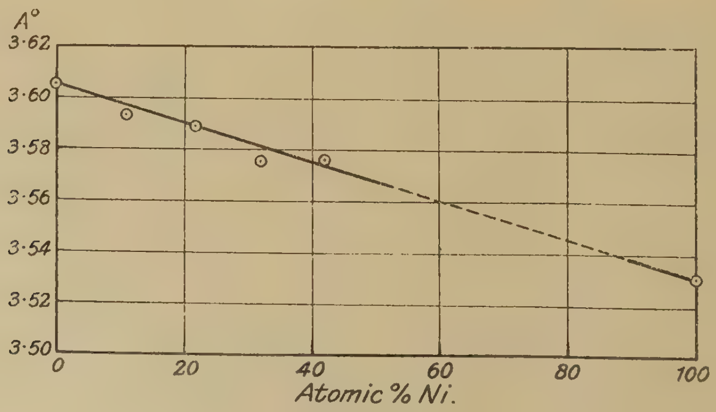


FIG. 8.

addition of nickel produces a small contraction in the copper lattice, the amount of the contraction being approximately a linear function of the atomic percentage of either component (*see* Fig. 8).

TABLE X.

Form.	10 % Ni.		20 % Ni.		30 % Ni.		40 % Ni.	
	Sin θ	a	Sin θ	a	Sin θ	a	Sin θ	a
111β	0·1512	3·593	...	...	...	...	0·1522	3·579
111α	0·1708	3·588	0·1711	3·582	0·1720	3·565	0·1716	3·573
100α	0·1962	3·609	0·1968	3·595	0·1973	3·586	0·1974	3·585
110α	0·2784	3·594	0·2784	3·594	0·2807	3·566	0·2804	3·570
222α	0·3412	3·592	0·3418	3·585	0·3421	3·583	...	...
Mean values		3·593Å		3·589Å		3·575Å		3·576Å

% Ni.	ρ grms./c.c.	M_s	$\sqrt[3]{\frac{4M_s}{\rho}}$	a	Diff.	$\sqrt[3]{\frac{4M_i}{\rho}}$		
0	8·93	63·57	3·608Å	3·605Å	−0·003	3·608Å	...	...
10	8·94	63·04	3·596	3·593	−0·003	3·736	...	...
20	8·95	62·53	3·587	3·589	+0·002	3·884	...	...
30	8·95	62·04	3·576	3·575	−0·001	4·061	...	...
40	8·92	61·53	3·571	3·576	+0·005	4·279	...	...

The value of the parameter of the lattice calculated from the density (as determined from rolled and annealed specimens) on the assumption that solution by substitution takes place is again in good agreement with the value of the parameter measured directly by the spectrometer. The last column of the lower half of Table X. contains the values of the parameter calculated on the interstitial theory. The departure of these figures from the observed values is very marked.

IV. CONCLUSIONS.

The foregoing results show that in solid solutions of copper-aluminium, aluminium-magnesium, and copper-nickel the solute atom replaces an atom in the lattice of the solvent. This substitution of atoms is accompanied in the cases examined by a distortion of the lattice, but the type of the lattice remains unaltered throughout a series of solid solutions until the limit of solid solubility is reached. In none of the cases examined was it found that the interstitial arrangement of atoms occurred, with the possible exception of copper-aluminium alloys rich in aluminium. In these alloys the atomic percentage of copper was so small that the accuracy of measurement was not sufficient to decide definitely between the two possible atomic arrangements.

Attention should be directed to the fact that in the lattice suggested for the intermetallic compound $CuAl_2$, the centres of the aluminium atoms are separated by 2·40 Å, which is smaller than the diameter of the atom (2·86 Å) deduced from the structure of pure aluminium. Similarly, the distance between the copper atoms, which is also 2·40 Å, is smaller than the atomic diameter of copper (2·54 Å) obtained from the pure element. A possible explanation of these results is that the atoms share electrons and are brought closer together than would otherwise be the case.

The facts accumulated as to the structure of Cu Al appear to indicate that this material is of the same nature as the solid solutions examined in this investigation. The trigonal lattice assigned to it is in reality a distorted lattice of the same type as that of the constituent elements ; it is similar, in fact, to the distorted lattice obtained in the case of copper-aluminium alloys rich in copper, but with a much more pronounced distortion. It is interesting to note that the material does not separate as Cu Al on solidification from the molten metal, but forms by diffusion in the solid state during prolonged annealing.

The results obtained with solid solution of aluminium in magnesium require explanation. One explanation which immediately suggests itself is that the aluminium atom in this instance is elongated, and that it takes its place in the magnesium lattice with its major axis along the hexagonal axis. It may be mentioned in this connection that Hull and others have found it necessary to assign shapes other than spherical to atoms to explain results obtained with certain crystals. We are at present extending the investigation to other alloys in the hope of obtaining further data on this point.

We wish to take this opportunity of thanking Dr. Rosenhain and the staff of the Metallurgy Department for supplying the specimens and for giving helpful advice throughout the course of the investigation.

DISCUSSION.

Mr. F. Twyman commented on the fineness of the definition in X-ray photographs, remarking that it might have been expected that owing to penetration of the rays into the material and from other causes considerable blurring would occur, yet the lines shown are not more than a hundredth of an inch wide.

Dr. E. A. Owen, in reply, said that the good definition might be ascribed (1) to the fact that the rays do not penetrate to any great depth in the reflecting material, owing to their being almost completely reflected by the outer layers of atoms ; and (2) to the well-known focussing effect obtained when the photographic plate and the source of radiation are equidistant from the reflecting surface.

THE FINE STRUCTURE OF SOME SODIUM SALTS OF THE FATTY ACIDS IN SOAP CURDS.

By S. H. Piper, *D.S.O., B.Sc., F.Inst.P.*, and E. N. Grindley, *B.Sc.*

(For text of Paper *see* Vol. 35, Part 5, August 15, 1923.)

Abstract.

X-ray photographs of certain sodium salts of the fatty acids (soap curds) show lines due to reflections from planes with very wide spacings of the order 40 A.U. These planar spacings increase uniformly with the number of CH_2 groups in the molecule, indicating an effective length of 1·25 A.U. for the CH_2 group. These and other lines can be accounted for by assuming that the curds are in the smectic state described by Friedel.

DISCUSSION.

Mr. G. Shearer said that in conjunction with Dr. Miller he had recently been examining compounds somewhat similar to those referred to in the Paper, with similar results. The compounds he had dealt with were, however, solids, namely the heavier fatty acids and their esters. He also had found a regular increment in the spacing for each CH_2 radicle added, and his observations confirmed the supposition that the axes of the molecules are perpendicular to the strata in which they lie. The experiments are of special interest in that they measure the actual length of one or of two molecules. He congratulated the Authors on the excellence of their photographs for a semi-liquid substance, which were exhibited at the meeting.

II.—SCATTERING OF LIGHT BY CARBON DIOXIDE, NITROUS OXIDE AND SOME ORGANIC VAPOURS.

By A. L. Narayan, *M.A.*, *A.Inst.P.*

Received March 1, 1923.

ABSTRACT.

It has been shown by Lord RAYLEIGH that the light scattered laterally by the molecules of gases is not completely polarised, but contains a component polarised at right angles to the direction which is predicted by theory for a spherical molecule, the two components being conveniently referred to as the " weak " and the " strong " components respectively. The Author was able to employ sunlight for illuminating gases and vapours, which he enclosed in a jointless tube. The strengths of the components were compared both by direct photometry and by photometric comparison of their effects on a photographic plate, improved thermo-electric apparatus being employed for the latter purpose. Lord Rayleigh's results were confirmed, particularly in the case of CO_2 and N_2O. It is suggested that the difference in the scattering power of these two gases is contrary to the prediction of the Lewis-Langmuir theory of the atom.

IN view of the fact that the results of careful experiments on scattering of light by different substances (both solids and fluids) will be of considerable value in testing the theories of molecular and atomic structure, the phenomenon of light-scattering has attracted the attention of many physicists and physical chemists in recent years. The work of the late Lord Rayleigh, and of his son the present Lord Rayleigh, have resulted in notable advances. On the Continent the subject has been studied by Cabbanes,* C. Fabry,† and Gans.‡ The results of various investigators are to a certain extent at variance with each other, Lord Rayleigh's§ values being consistently higher than those of the other observers. Recently W. H. Martin|| has studied the scattering of light by dust-free liquids, and sought to measure the relative intensities and polarisation of the light scattered by various liquids, and to find in the case of binary mixtures if the amount of scattering was an additive property. As was pointed out by the late Lord Rayleigh and by Fabry, the theory of molecular scattering explains some of the phenomena of irridescent colouring often met with in the organic world, and leads to an explanation of a great variety of astro-physical problems, such as the varying luminosities of the cometary appendages, the zodiacal light, the solar corona, &c. The present Lord Rayleigh and Cabbanes by photographic photometry independently verified with considerable precision the relation between the intensity of light scattered laterally and the number of molecules. Since the appearance of Martin's Paper on the subject further investigations have been conducted in this laboratory, which in general appear to confirm Martin's results in the case of liquids.

---

* Comptes Rendus, 168, pp. 340-43, February 17 (1919).

† Nature, 100, p. 473 (1918), and J. de Physique, pp. 89-102 (1917).

‡ Ann. de Physik, 65, pp. 97-123, May 31 (1921), and Science Abstracts, Sec. A, 1677 (1921).

§ Proc. Roy. Soc., Vol. 95, p. 155 (1918), and Vol. 97, p. 435, August (1920).

|| J. Phys. Chem., 26, pp. 75-88, January (1922).

Recently, Prof. Rankine, in an interesting Paper on the similarity between carbon dioxide and nitrous oxide (Proc. Roy. Soc., February 2, 1921), pointed out that one of the most remarkable evidences in favour of Lewis and Langmuir's theory of molecular constitution is the close degree of equality between nearly all the physical constants of the two gases, which behave not merely as though the molecules had the same size and shape, but as if each of them had an external electron arrangement practically the same as that of three Neon atoms in line.

Again, the theory of molecular scattering indicates that the scattering of light arising from molecular anisotropy affords a good test of the molecular model. The experiments of Lord Rayleigh show that the intensity of the weak image compared with that of the stronger is 11·7 and 15·4 per cent. in CO_2 and N_2O respectively. As these results would appear to be in conflict with what we should expect from the similarity of the two gases it was considered mecessary that experiments should be repeated with these gases, and the results either confirmed or disproved. The following experiments were therefore undertaken originally with a view to studying the scattering of light by these two gases, and especially to find the intensity of the weak image compared with that of the stronger. On completion of these experiments, on account of the extreme reliability and sensibility of the photometric method adopted, experiments were continued with some organic vapours like ether, benzene, &c., in which case considerable difficulty is generally experienced in maintaining the enclosed vapour at a high degree of purity on account of the action of the vapour on the cement at joints. As will be seen from the description given below, the experimental tube in these experiments is of the type recommended by Prof. Wood, and is free from all joints.

On account of the very brilliant sunlight obtainable in these parts, and on account of its fairly constant nature from 11 a.m. to 2 p.m., sunlight was used as the source of light in all these experiments, in preference to the arc-light, which is liable to random and oftentimes sudden variations amounting to 30 to 50 per cent. of the mean value.

Although for the experiments on carbon dioxide and nitrous oxide branched metal tubes as used by the present Lord Rayleigh could be used with advantage, difficulties were experienced in arranging a tube of this type so that there was a completely dark background; it was also feared that in the case of vapours of organic substances the vapours might absorb the black paint inside the tube and give rise to contamination. It was therefore deemed advisable to use the type of tube recommended by Prof. Wood for the investigation of rare gases. The tube was made entirely of glass, and was of the form shown in Fig. 1, the dimensions of the tube being nearly 30 cm. in length, and 3 cm. in diameter. The tube was first thoroughly cleaned and dried. In order to obviate the back reflection or light from the bottom of the dark cave which the other end of the tube formed it was drawn out as shown at *A*; and three large bulbs were blown at *B*, *C* and *D*.

In the cases of CO_2 and N_2O pure dry gas was passed through a tube containing densely packed cotton, and thence into the experimental tube, for about half an hour, to ensure that it was filled with pure, dry and dust-free gas; the side-tubes were then hermetically sealed. In the case of vapours a small quantity of the liquid was introduced into the tube, and the whole was warmed in a flame. When the jet of vapour issued from the side tubulure, after waiting for a few minutes, it was hermetically sealed. In all cases, the whole tube, with the exception of narrow rectangular patches on the two bulbs C and D and a circular patch on the observation bulb B, was given four or five coatings of thick black paint. In order to ensure complete darkness the tube was further enclosed in a deal-wood case, painted inside with dead black paint. Opposite to the bulbs B, C, D small apertures were made on the sides of the box so as to admit the beam of sunlight. When the arrangements were complete one of the side-holes D could be closed by a sliding shutter, the inside surface of which was coated with black paint. In order to obviate the diffused light the tube was made to pass through a number of diaphragms made of black paper.

As has already been pointed out, sunlight was used as the source of light, a beam being directed into the dark room through a hole in one of the shutters by means of a heliostat mounted on the balcony outside, and kept in motion by clock-work. The beam of light was brought to a focus by means of a cylindrical lens at the centre of the experimental tube, i.e., midway between the two bulbs, C and D; before being admitted into the tube it was made to pass through a rectangular diaphragm, so as to limit the area to be photographed on the scattered beam. Between the hole in the shutter of the dark room, and the experimental tube were interposed a number of black cardboard diaphragms with openings for the beam of light.

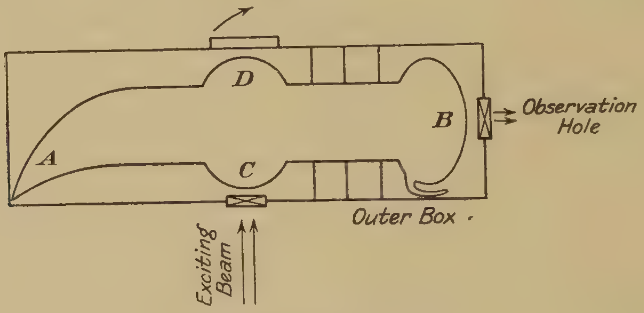


FIG. 1.—EXPERIMENTAL TUBE.

The arrangement adopted for examining the degree of polarisation in the laterally scattered light was the same as in the Cornu Polarimeter, the important parts being a rectangular opening, a double image prism, and a large nicol attached to a divided circle. First the position of the double-image prism was adjusted so that the two images of the rectangular opening were seen side by side through the nicol. The double-image prism and the nicol were set in two positions successively, for which the intensities of the two halves of the field appeared equal. Then the percentage of polarisation is given by $P=100 \sin (W''-W')$. On account of the extreme brilliance of the exciting beam in these experiments, careful settings of the nicol prism were first made by eye-observations in order to obtain equality of illumination. About this position a number of photographs were then taken for slightly different readings on the divided circle of the nicol prism, and subsequently by photometric examination the best reading was selected.

In all these experiments Wratten and Wainwright allochrome plates, 3 × 9 cm., were used for photographing the scattered light, a Ross tele-centric lens being used with the camera. Before the photographic arrangement was adopted a large number of eye-observations were made in all these cases.

*Photometric Arrangement.**

In order to compare the photographs, a linear thermopile and Paschen Galvanometer were used in these experiments, instead of the photo-electric method adopted by Lord Rayleigh. Fig. 2 represents the optical arrangement adopted for comparing the photographs, and it is more or less similar to the arrangement adopted by Nagaoka & Takamine in their experiments on the constitution of mercury lines (Proc. Phys. Soc., Vol. 25), and to that adopted more recently by Dr. Moll in his micro-photometer. Light proceeding from a straight metal-filament lamp was focused by means of the condenser *C* of a lantern on a slit *S′*, and a greatly-reduced image of this slit was thrown on the photographic plate by means of a short-focus lens (in fact a microscope objective was used) *L′*; another lens, *L″*, forms an enlarged image of this plate on the slit *S″*, behind which

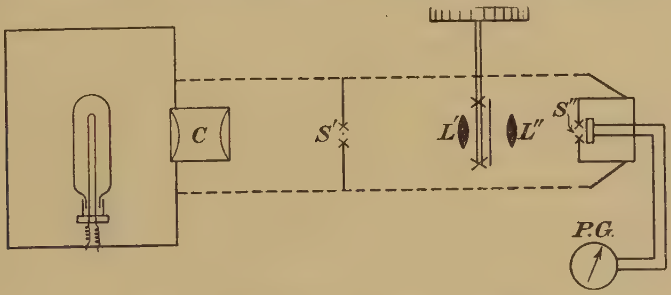


Fig. 2.—Photometric Arrangement.

there is the linear thermopile made by Adam Hilger & Co. for use with the mirror-spectrometer in radiometric investigations. The thermopile was made of bismuth-tin and bismuth-antimony alloys, and the number of junctions was 20. The whole thermopile was enclosed in an outer nickel box stuffed inside with absorbent cotton, and surrounded outside with pads of similar stuff; and by means of suitable leads it was connected to a Paschen galvanometer. The photographic plate was mounted on one of the uprights of an optical bench furnished with a micrometer-screw with transverse motion.

These experiments clearly show that the light scattered laterally in all these cases was not completely polarised, but that there was a residual defect, and the measurements of depolarisation for the various gases and vapours experimented upon are given in the following table, which shows that they are in remarkable agreement with those of Lord Rayleigh in the case of carbon dioxide and nitrous oxide. But in the case of organic vapours, there is some difference between these results and those of Lord Rayleigh, which might possibly be due to some unavoidable contamination in Lord Rayleigh's experimental tube. As the tube used in the present experiments is free from the defects of joints of metal tubes, tubes of this type would appear to be much better for the study of light-scattering by organic vapours.

---

* Though such a high degree of refinement is not necessary in a photometric arrangement, ce the author had no photo-electric cell at his disposal, and as this photometer was set up by i in connection with experiments on the satellites of 1, *s*—*m*, *p* of potassium, the same arrange-nt was adopted here.

Gas or Vapour.	Intensity of weak component (per cent. of stronger).	Lord Rayleigh's values.
Carbon dioxide	10·9	11·7
Nitrous oxide	14·9*	15·4
Ether vapour	2·1	1·7
Benzene	8·0	6·0
Chloroform	5·0	3·0
Carbon disulphide	14·2	12·0

* 15·8 for another set of experiments.

Further, the experiments on the scattering power of these different vapours show that the intensity of the scattered light is only roughly proportional to the square of the refractivity of the substances.

My thanks are due to Mr. D. Gunnayya, M.A., of the Physics Department, who kindly prepared the experimental tubes for me.

DISCUSSION.

Prof. A. O. Rankine said that his experiments, referred to in the Paper, merely showed that the collision-area of the molecules in question varies with orientation in a manner consistent with the Lewis-Langmuir theory ; it may conceivably be possible to invent other molecular models with which the experimental results will be equally consistent. These results, however, are relevant only to the external form of the molecules, for viscosity may be presumed to be unaffected by the distribution of mass between the nuclei. Thus the masses of the nuclei would, according to theory, be 8, 6, and 8, in CO_2, and 7, 8, and 7, in N_2O ; and since, as Sir J. J. Thomson has suggested, these molecules would have different moments of inertia though their masses would be equal, it might be expected that they would differ in their polarising effect.

Mr. J. Guild said that in the measurement of such small intensities of light a large experimental error must be expected, so that the agreement between the Author's and Lord Rayleigh's results was much better than might have been expected. Particularly in the case of vapours, where the percentage of the " weak " component is small, the Nicol system is being used under the most disadvantageous conditions, which are calculated to evoke various defects even in the most perfect apparatus. As regards the photographic method of photometry, would not the actinic effects of the " strong " and of the " weak " components be different ? In the case of the Tyndall effect due to larger aggregates, the intensities of the corresponding components are respectively proportional to the inverse fourth and the inverse eighth powers of the wave length, so that the " weak " component would be much bluer than the " strong " and have a disproportionate effect on the plate. The Author mentions that many iridescent colours in Nature are due to scattering of light. It is interesting to note that many other common colours have been traced to the same cause, e.g., the blues of the sky, of bird's feathers, and of the eyes of blondes.

Lord Rayleigh, in reply to the discussion, said that he did not suppose the authors of the Lewis-Langmuir theory regarded their model as a real representation of the atom, consistent with all the latter's properties. It is rather a schematic diagram adapted to summarise certain groups of these properties, and might well be inconsistent with other such groups. The chromatic difference between the components in the Tyndall effect, though not completely accounted for, is a fact ; but the effect is not comparable with that under discussion, the smallest particles which show the Tyndall effect being large compared with molecules. That there is no substantial chromatic effect on the photographic plates is proved by the agreement of the results of the photographic method with those of direct photometry.

III.—ON THE MEASUREMENT OF THE SURFACE TENSION OF A SMALL QUANTITY OF LIQUID.

By Allan Ferguson, *M.A., D.Sc.*

Received June 8, 1923.

Abstract.

If a small quantity of liquid—one cubic millimetre or less—be placed in a vertical capillary tube, its surface tension may be determined by applying pressure to the upper end of the tube, and measuring the pressure necessary to force the liquid into such a position that the meniscus at the lower end of the tube is *plane*.

Interfacial tensions may also be determined in this way.

If no restriction be placed on the amount of liquid available, a simple apparatus may be used by means of which the ordinary surface tension of a liquid, or the interfacial tension between two liquids, may be measured in several different ways.

THE precise determination of the surface tension of a *very* small volume of liquid —of the order, say, of one cubic millimetre—has not, so far as I know, received much attention; the measurement of the tension at the interface of two small portions of liquid has not been attempted at all. Fairly accurate values of the tension at a liquid-air surface may be obtained by measuring the period of oscillation of a small drop of the liquid, but the method is hardly likely to commend itself for widespread use, especially in technological laboratories.

Kiplinger* has attempted measurements by placing a thread of liquid in a vertical capillary tube open at both ends; the capillary is then inclined until the meniscus at the lower end of the tube is plane, when the surface tension is given by

$$T = \frac{rl\rho g \cos \alpha}{2},$$

where α is the angle of inclination of the capillary to the vertical. The results obtained do not possess much quantitative value, being uniformly about 4 per cent. too low. Part of this error is probably due to the fact that it is impossible in an inclined tube to obtain an accurately plane meniscus.

The necessity, in experiments of the capillary-rise type, for the use of relatively large quantities of liquid is due to the fact that the surface of the liquid in the communicating vessel (Fig. 1(*a*)) must be, to a high degree of approximation, plane, and this demands the use of a vessel not less than about 4 centimetres in *diameter*.

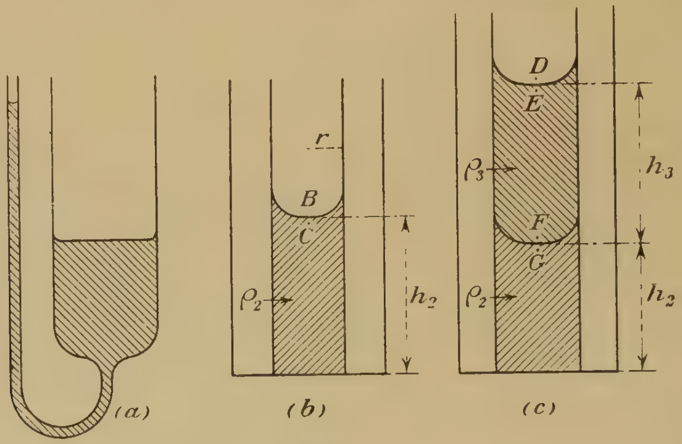
If we could measure the radius of curvature at the vertex of the meniscus of the liquid in the communicating vessel with any high degree of accuracy it would be possible, by employing a tube of, say, 1 cm. bore, to minimise the quantity of liquid used. Unfortunately, the analysis which gives the necessary corrections to the simple theory demands that r/h—where r is the radius of the tube, and h the height to which the liquid rises in the tube—shall be either very small, or very large, compared with unity, and breaks down over a range which includes tubes of moderate bores.

Many years ago Bashforth and Adams† published a valuable series of tables which made it possible to calculate accurately the shapes of capillary surfaces of revolution of all sizes. It is a matter for regret that these tables should have lain so long unused, and it is only quite recently that Sugden* has employed them to calculate the radius of curvature at the vertex of the meniscus in a relatively small containing vessel. He has thus determined accurate values of surface tensions employing only a few cubic centimetres of liquid.

---

* Jour. Amer. Chem. Soc., 42, 472 (1920).

† "An Attempt to Test the Theories of Capillary Action" (Camb. Univ. Press, 1883).



(a) (b) (c)

Fig. 1.

The method now to be described demands the employment of much smaller quantities of liquid than is contemplated by the methods of Kiplinger or Sugden.

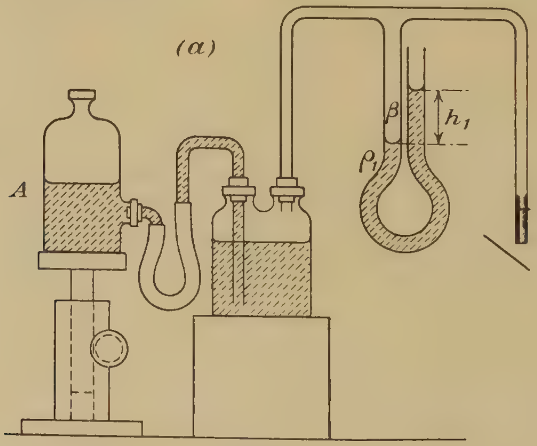


Fig. 2.

Indeed the quantity necessary may be no more than is required, in a mm. or $\frac{1}{2}$ mm. tube, to form a concave meniscus at one boundary of the liquid and a plane meniscus at the other, the shortest distance between the two bounding surfaces being greater than the range of molecular forces.

---

* Jour. Chem. Soc., 119, 1483 (1921).

The simple apparatus required is shown in Fig. 2, which almost explains itself.

A very short thread of the liquid is contained in a vertical capillary (shown enlarged in Fig. 1(*b*)). The capillary is connected to a pressure-apparatus and a manometer, and, by raising the vessel *A*, the thread of liquid is forced down the capillary until the meniscus at the open end is accurately plane.

The planeness of the meniscus may be judged by examining, with a hand lens, the image in the meniscus of the filament of a small 10-volt lamp placed obliquely under the capillary at a distance of 30 or 40 cm. away. For convenience in viewing the end of the tube, a plane mirror is placed near the end of the tube at an angle of 45 deg., so that the capillary as viewed in the mirror appears to be horizontal. As the pressure is slowly increased until the meniscus becomes plane, the image broadens out into a pool of light, reappearing if the mark be overshot.

(The setting is quite sensitive; thus in one series of experiments, twenty settings were made, and twenty corresponding readings of the manometer taken. Equation (4), following, shows that the quantity $(\rho_1 h_1 + \rho_2 h_2)$ should be constant. The mean value of this constant was found to be

$$1{\cdot}200 \pm 0{\cdot}003 \text{ cm.},$$

showing a probable error of about 0·3 per cent. This is sufficiently accurate when we remember that no special precautions were taken to keep the temperature constant.)

A reading of the pressure required to make the meniscus plane then gives the surface tension of the liquid.

Shorn of all corrections the theory is quite simple. If Π be the atmospheric pressure, then (Fig. 2 and Fig. 1(*b*))

$$P_c = \Pi - g\rho_2 h_2$$

and

$$P_B = P_c + \frac{2T}{R},$$

where *R* is the radius of curvature of the meniscus at its vertex; also

$$P_B = \Pi + g\rho_1 h_1,$$

and therefore

$$\Pi + g\rho_1 h_1 = \Pi - g\rho_2 h_2 + \frac{2T}{R}.$$

Hence

$$T = g\frac{R}{2}(\rho_1 h_1 + \rho_2 h_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If the radius r of the tube be so small that r/h—where h is the height to which the liquid would ascend in the tube—is very small compared with unity, then, very approximately

$$R = r/\cos\alpha$$

giving

$$T = \frac{gr}{2\cos\alpha}(\rho_1 h_1 + \rho_2 h_2). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If in addition we assume the contact angle α to be zero, we have

$$T = \frac{gr}{2}(\rho_1 h_1 + \rho_2 h_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

I have elsewhere* shown that for a liquid of zero contact angle we have as a second approximation

$$R=r\left(1+\frac{r^2}{6a^2}\right),$$

where, as usual, $a^2 \equiv T/g\rho_2$.

If we substitute this expression for R in the *exact* equation (1), we find, after a few simple reductions that

$$T=\frac{gr}{2}(\rho_1 h_1+\rho_2 h_2)+\frac{g\rho_2 r^2}{6}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

This, which we use as our working equation, is sufficiently exact for the tubes ordinarily used in experiments of this type.

If we are dealing with interfacial tensions the calculation proceeds on similar lines.

The two liquids are superposed as in Fig. 1 (*c*), and the pressure is measured which is required to make the lower meniscus exactly plane.

Clearly, we have (Figs. 2 and 1(*c*))

$$P_D=\Pi+g\rho_1 h_1,$$

and from Fig. 1(*c*)

$$P_D=P_E+\frac{2T_3}{R_3}$$

$$P_E=P_F-g\rho_3 h_3$$

$$P_F=P_G+\frac{2T_{23}}{R_2}$$

$$P_G=\Pi-g\rho_2 h_2$$

leading to the *exact* equation

$$\frac{2T_{23}}{R_2}=g(\rho_1 h_1+\rho_2 h_2+\rho_3 h_3)-\frac{2T_3}{R_3}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

If we now make the second order corrections for the two surfaces concerned, we find after a few reductions that

$$T_{23}=\frac{gr}{2}(\rho_1 h_1+\rho_2 h_2+\rho_3 h_3)+\frac{g\rho_2 r^2}{6}-T_3. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

I now give a few figures, which I owe to the kindness of Miss W. Rolton and Mr. R. S. Troop, showing the results of experiments made to determine the surface tensions of benzene, of water, and of a benzene-water interface. The benzene used was free from thiophene, and was of "research" quality. As the production of authoritative figures for the surface tensions involved forms no essential part of this Paper, which is simply intended to illustrate the consistency and sensitiveness of the method, the benzene employed was used as it came from the retailer without further purification.

The manometer for the pressure readings was of the simple U-tube form, and was read by a cathetometer provided with a vernier reading to $\frac{1}{50}$ mm. In the earlier experiments water was used as the indicating liquid; but the London atmosphere appeared to affect the exposed meniscus, and aniline was later substituted for the water, with marked effects on the consistency of the readings.

---

* Manchester Memoirs, lxv., No. 4 (1921); Trans. Far. Soc., February (1921).

It is hardly necessary to give the readings in full detail. The important quantity is $(\rho_1 h_1 + \rho_2 h_2)$, which, at constant temperature, should be constant.

One series of 28 readings taken on benzene, using a capillary of radius 0·0480 cm., gave the following values :

$$\rho_1 h_1 + \rho_2 h_2 (\text{gm.-cm.}^{-2})$$

1·202,	1·245,	1·234,	1·255,	1·214,	1·208,	1·209
1·171,	1·233,	1·219,	1·223,	1·192,	1·193,	1·189
1·211,	1·221,	1·203,	1·142,	1·163,	1·209,	1·174
1·193,	1·191,	1·189,	1·192,	1·203,	1·178,	1·181

The mean of these gave

$$\rho_1 h_1 + \rho_2 h_2 = 1{\cdot}200 \pm 0{\cdot}003 \text{ gm.-cm.}^{-2},$$

leading to a surface tension of 28·58 dyne-cm.$^{-1}$ at 20·2°C.

A second series of 10 readings with a tube of radius 0·0400 cm. gave

$$\rho_1 h_1 + \rho_2 h_2$$

1·446,	1·447,	1·470,	1·464,	1·470
1·462,	1·438,	1·461,	1·470,	1·461

The mean is 1·459 gm.-cm.$^{-2}$, giving a surface tension of 28·87 dyne-cm.$^{-1}$ at 16·0°C.

The mean of these two values, reduced to 15°C., using the known value of the temperature coefficient, gives

$$T_{15} = 29{\cdot}20 \text{ dyne-cm.}^{-1}.$$

For convenience of comparison, a short table is appended, which shows a few of the results obtained by other methods.

TABLE I.

Experimenter.	Method.	T_{15}
Volkmann	Capillary rise	29·51
Harkins and Brown	Capillary rise	29·59
Ramsay and Aston*	Capillary rise	28·68
Renard and Guye	Capillary rise	28·45
Richards and Coombs	Capillary rise	29·61
Ferguson	Jaeger's method... ...	29·65
Feustel	Jaeger's method... ...	30·90
Ferguson and Dowson...	Capillary pressure ...	29·66

* This value is for the surface tension of benzene in contact with its saturated vapour.

A similar series of five sets of experiments carried out on water gave the following results :—

TABLE II.

S. tension in dyne-cm.$^{-1}$.	Temp. in °C.
72·44	17·2
72·72	18·5
71·90	20·3
72·37	20·8
72·42	19·6

If we reduce these values to 15 deg. we find as mean value

$$T_{15}=73{\cdot}05 \text{ dyne-cm.}^{-1}.$$

It is noteworthy that in some of these experiments the quantity of liquid employed was as little as 0·00096 cub. cm.

Table III. shows a number of values of T_{15} obtained by different methods, and it will be seen that the value given above lies well within the limits of the table, differing by about 0·5 per cent. from Proctor Hall's figure, which is probably one of the most reliable values.

TABLE III.

Observer.	Method.	T_{15}
Volkmann	Capillary rise	73·26
Domke	Capillary rise	73·46
Hall	Weighing tension in film	73·45
Sentis	Capillary tube	73·76
Dorsey	Ripples	73·72
Bohr	Waves on jet	72·78
Ferguson	Pull on sphere	73·45
Kalähne	Rippled surface used as diffraction grating	74·22

Finally, two groups of determinations of the interfacial tension between benzene and water gave 34·46 dyne-cm.$^{-1}$ at 19·2°C. and 34·02 at 20·2°C.

If we assume from the results of Harkins and Brown's experiments a temperature coefficient of 0·06 dynes per centimetre per degree centigrade, we have, as a mean value,

$$T_{20}=34{\cdot}22 \text{ dyne-cm.}^{-1}.$$

There are not many comparison figures available. Harkins and Brown* give

$$T_{20}=34{\cdot}52 \text{ dyne-cm.}^{-1}$$

and Reynolds†

$$T_{20}=34{\cdot}34 \text{ dyne-cm.}^{-1}.$$

Both these values have been obtained by the capillary rise method.

As a matter of experimental procedure it is worth noting that, for ordinary tutorial purposes, it is convenient to fasten the capillary on to the pressure part of the apparatus by means of a piece of rubber tubing. The capillary may then be easily removed for the purpose of cleaning, and may be used with the "plane-meniscus" end pointing either upwards or downwards. For research purposes it is advisable to fuse the capillary on to the rest of the apparatus.

If the supply of liquid be not restricted a simple modification of the design of the apparatus as shown in Fig. 3 provides one with what may be called a surface tension *multum in parvo*, enabling one to measure both ordinary and interfacial tensions in several different ways.

Thus, the apparatus can obviously be used for the ordinary capillary rise experiment. By connecting it up to the pressure gauge one can measure the pressure required to pull the meniscus down to the lower end of the tube—a method which have described elsewhere,* and which has several advantages. Decrease the ressure still more until bubbles of air are *slowly* detached, and we have a deternination by Jaeger's method.

---

* Jour. Amer. Chem. Soc., 41, 499 (1919).

† Jour. Chem. Soc. 119, 460 (1921).

Now suppose that we *increase* the pressure until the meniscus is forced up to mark near the upper end of the tube and distant, say, h cm. from that end. Force he liquid up still farther until the meniscus is plane at the upper orifice and measure he *excess* pressure necessary to effect this. If h_1 be the excess head on the manoneter, then, small corrections neglected,

$$T=\frac{gr}{2}(\rho_1 h_1-\rho h)$$

If instead of air in the upper part of the capillary we have a column of another iquid of length h_3 and density ρ_3, then if we measure the pressure required to make the upper meniscus of the upper column plane at the orifice of the tube, we asily see that the interfacial tension (T') between the two liquids is given by

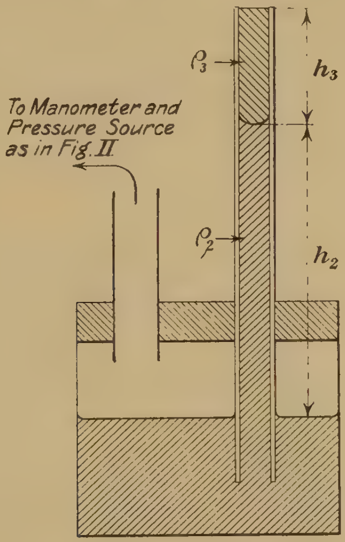


FIG. 3.

$$T'=\frac{gr}{2}(\rho_3 h_3+\rho_2 h_2-\rho_1 h_1),$$

where h_1 is the manometer head, and h_2 the length of the lower column of liquid n the capillary.

Hence we can make a determination of the interfacial tension T' without the ecessity of knowing the ordinary surface tensions of either of the two liquids oncerned.

These experiments were made in the Department of Physics in the East ondon College; my thanks are due, and are tendered, to Professor Lees, who has aken much interest in the progress of the work, and has given every facility for its ompletion.

---

* Ferguson, *l.c.*

DISCUSSION.

Mr. R. H. HUMPHRY (communicated) : It will be seen, from equation (4) that the evaluation of T requires a knowledge of ρ_1 and ρ_2 as well as h_1 and h_2. When only a small volume of liquid is available, say, 1 cubic millimetre, the value of ρ_2 may be in serious error. Dr. Ferguson does not mention the accuracy required in this determination. It would be interesting to know with what accuracy ρ_2 can be determined and the consequent error in the determination of T.

Dr. D. OWEN, referring to the measurement of surface tension at the interface of two liquids asked if any difficulty was met in introducing the latter into a capillary tube without rendering the meniscus indistinct. It would be interesting to know the degree of consistency between the results of repeated experiments.

Mr. T. SMITH queried the figure given for the probable error in the observations on benzene.

The AUTHOR, in reply to the discussion, said that by using a very small quantity of the liquid under observation it was possible to render negligible the effect of errors in the density attributed to it. This density can even be made to disappear from the equations by using a horizontal capillary tube, if the diameter of the latter be small enough to obviate the distortion of the meniscus by gravity. No difficulty had been experienced in obtaining a clear-cut meniscus with immiscible liquids, and the consistency of repeated experiments is fairly illustrated by the figures for benzene. He believed that the probable error had been correctly calculated, but would check it.

[Added Nov. 22nd, 1923. The probable error has been checked, both by the ordinary formula and by Peters' formula, and remains as given in the text.]

DEMONSTRATION OF REPRODUCTION OF VOWEL SOUNDS.

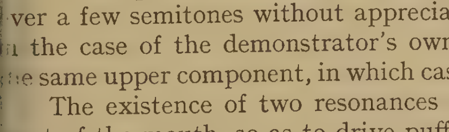
By Sir Richard Paget, *Bt.**

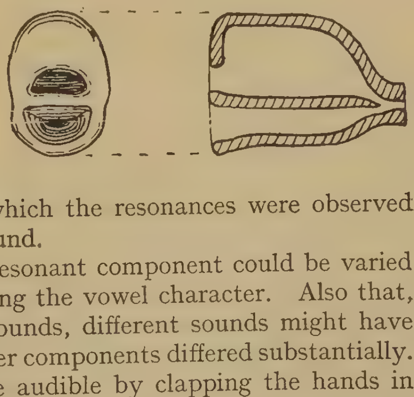
Abstract.

The author has found that each of the whispered vowel sounds comprises two characteristic udible resonant components. Each component may vary over a range of a few semitones, and he upper and lower components are separated in the case of different vowels by intervals of rom about 36 to 6 semitones. The voiced vowels are produced by passing vibrating air (from he larynx) through the oral cavity when adjusted to give the approximate pair of resonances. he devices shown for reproducing vowels consisted in their simplest form of pairs of resonators uned to the tones characteristic of various vowels and so arranged that the sound from an rtificial larynx or squeaker could be passed through them in series or in parallel. Certain vowels ı which the upper resonance is a harmonic of the lower can also be produced by means of a ngle resonator. The author, in illustration, arranged his hands to form a double resonator in nitation of the human mouth, and passed through them the sound from a squeaker representing he larynx. By manipulating the fingers and hands, he was able to pronounce the various vowel ounds, and some recognisable sentences.

OBSERVATION of the resonances of the demonstrator's own vocal cavity, when whispering or breathing the various English vowel sounds, had shown hat, in the case of every vowel, the vocal cavity produces two audible resonances, lue to the passage of air through the cavity as a whole.

The actual resonances recorded were shown on a chart in which (*see diagram*) he vertical scale represents semitones of the equal-temperament scale and the hick vertical lines represent the ranges over which the resonances were observed o vary at different trials of the same vowel sound.





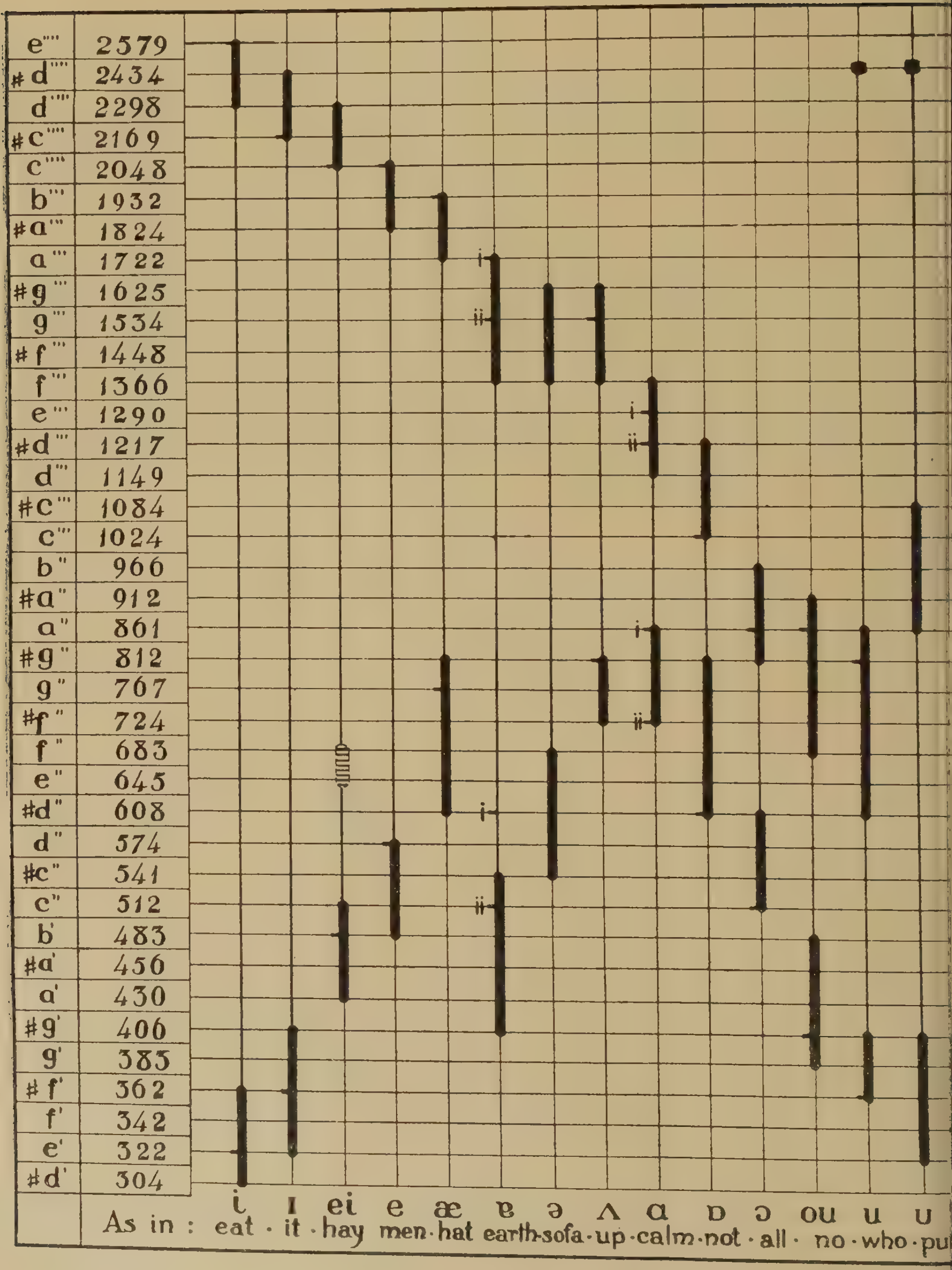
It was pointed out that the pitch of each resonant component could be varied ver a few semitones without appreciably altering the vowel character. Also that, n the case of the demonstrator's own vowel sounds, different sounds might have e same upper component, in which case the lower components differed substantially.

The existence of two resonances was made audible by clapping the hands in ont of the mouth, so as to drive puffs of air into the vocal cavity. It was shown at two resonances can be varied independently, so as, e.g., to make two audible cales in contrary motion.

Experiments with plasticine models showed that the vocal cavity behaved bstantially like two Helmholtz resonators joined together in series. In this

---

* "Vowel Resonances," by Sir Richard Paget, Bt. (International Phonetic Associatio 922); Proc. Roy. Soc., A., Vol. 102, p. 752 (1923).


e'''' 2579
#d'''' 2434
d'''' 2298
#c'''' 2169
c'''' 2048
b''' 1932
#a''' 1824
a''' 1722
#g''' 1625
g''' 1534
#f''' 1448
f''' 1366
e''' 1290
#d''' 1217
d''' 1149
#c''' 1084
c''' 1024
b'' 966
#a'' 912
a'' 861
#g'' 812
g'' 767
#f'' 724
f'' 683
e'' 645
#d'' 608
d'' 574
#c'' 541
c'' 512
b' 483
#a' 456
a' 430
#g' 406
g' 383
#f' 362
f' 342
e' 322
#d' 304
i
ii
i
ii
i
ii
i
ii
i ɪ ei e æ ɐ ə ʌ ɑ ɒ ɔ ou u ʊ
As in : eat · it · hay men · hat earth · sofa · up · calm · not · all · no · who · pu

arrangement the human tongue acted as a variable and longitudinally moving stop, so as to divide the vocal cavity as a whole into two resonators each of the appropriate pitch.

A series of plasticine resonators giving the vowel sounds a (as in calm), e (as in men), i (as in it), ɔ (as in all) and u (as in who) were exhibited on the late Lord Rayleigh's experimental organ, lent by the Royal Institution.

In these models the function of the human larynx was performed by an organ pipe reed.

Other models giving i (as in eat), æ (as in hat), ʌ (as in up), ɒ (as in not), and ou (as in no), and in which the artificial larynx consisted of a rubber strip, were blown by mouth.

It was shown that vowel sounds could also be produced by two Helmholtz resonators in parallel and energised by a single reed. A model giving i (as in eat) and energised by an organ reed was demonstrated on the organ, and models giving ʌ (as in up) and u (as in who) and energised by a rubber strip reed were blown by mouth.

A recognisable vowel sound—ɔ (as in all)—was produced by blowing a model having a larynx interposing between two resonators, so that the energising air passed first into the one resonator, then through the larynx, and then through the second resonator.

It was pointed out that this experiment indicated that resonance in the human wind-pipe might have an appreciable bearing on vowel-sound production.

Certain vowels could be satisfactorily produced by means of a single cylindrical resonator, and the production of the vowel ɐ (as in earth) was shown by blowing a cylindrical plasticine resonator energised by a rubber strip reed.

It was pointed out that in this case the resonator gave its fundamental note and a second audible resonance, of three times the frequency of the fundamental, and by reference to the chart it was seen that the resonances of the vowel sound ɐ (as in earth) had a frequency relation of about 3-1.

Experiments were shown on the production of changing vowels, produced by varying the resonances of a double resonator.

A plasticine double resonator was shown energised by a diaphragm of a motor orn ("Clear Hooter") which gives a relatively pure note. The resonators and he orifice between them were so proportioned as to give approximately the vowel ound ei (as in hay). By partially closing the mouth of the resonator by hand the esonances were progressively changed to those of ɐ (as in earth), u (as in who), and ack to ei, so as to give the word "away."

A cylindrical metal resonator was shown having a longitudinally moving erforated stop, by which the resonance could be changed from those of i (as in at) to ɔ (as in all). This variable resonator, which was also provided with a iding reed stop so as to vary the pitch of the reed note, was made to sound ee-aw."

A simple form of hand-operated talking machine, or Cheirophone, was shown, n which the larynx consisted of a single rubber strip, of which the pitch could be aried over an octave or more, by varying the air pressure, while a double resonator as formed by the operator's hands.

In this arrangement the "pharynx" tube of the artificial larynx was held etween the thumb and first finger of one hand, the other three fingers of which operated as a tongue, while the thumb and first finger of the other hand operated as the variable opening or lips of the front resonator.

It was shown that by this device the various vowel sounds could be recognisably reproduced, as well as a number of spoken words, such as " Hulloa," " How are you," " Hip, hip, hip, hurrah," and " Oh ! I love London."

The illustrations on pages 45 and 46 are reprinted by kind permission of the Royal Society.*

DISCUSSION.

Mr. D. J. Blaikley inquired whether Sir Richard considered that the space between the true and the false vocal chords has any influence on pronunciation.

Dr. E. H. Rayner inquired whether the vowel resonances are affected by age and sex.

Mr. A. G. Shrimpton inquired whether the vowel resonances depend on the pitch of the fundamental.

Sir Richard Paget, in reply, said that a short length of tubing between a " larynx " and a compound resonator affects the character of the sound emitted, so that the answer to Mr. Blaikley was in the affirmative. The difference between deep and shrill voices depends primarily on the length of the vocal chords, and in order to give the vowel resonances without sacrificing that required by the fundamental, the compound resonator formed by the mouth as a whole has to be shorter in the case of shrill voices. When the fundamental is two or three octaves below the vowel resonances, the latter are unaffected by variation in pitch of the former ; but when the difference is of the order of an octave, the vowel resonances vary slightly within their characteristic ranges in such a way as to coincide with some harmonic of the fundamental.

Proc. Roy. Soc. A., Vol. 102 (1923), Diagram p. 753, Fig. 20 p. 762, Fig. 22, p. 765.

IV.—X-RAY ANALYSIS OF ZINC-COPPER ALLOYS.

By E. A. Owen, *M.A., D.Sc.*, and G. D. Preston, *B.A.*,

The National Physical Laboratory.

Received November 9, 1923.

Abstract.

(1) Alloys containing up to 38 per cent. zinc constituting the α brasses are found to possess a face centred cubic lattice, the parameter increasing from 3·608 Å for pure copper to 3·696 Å for an alloy containing 38 per cent. zinc. Solution takes place by the substitution of zinc atoms for copper atoms.

(2) (*a*) The X-ray analysis of a brass containing 48·5 per cent. zinc by weight showed that the β brasses possess a centred cubic structure, the side of the unit cube being 2·946 Å.

(*b*) Specimens quenched from 550° C. and annealed below 470° C. gave identical spectra and showed no sign of the presence of the α phase. The evolution of heat observed at 470°C. is not accompanied by a change of crystal structure, and is similar to the α-β transformation in iron. It is not accompanied by a breaking up of the β constituent into a mixture of α and γ.

(*c*) Specimens containing 43·7 per cent. zinc by weight were examined. The first annealed at 750° C. and quenched showed the reflections due to β brass only. The second annealed at 500° C. and quenched, and the third annealed at 400° C. consisted of a mixture of the α and β phases. The results of X-ray analysis are in agreement with the constitutional diagram of Shepherd.

(3) The γ phase is found to crystallise on a rhombohedral hexagonal structure of side 4·136 Å and axial ratio 0·6495.

(4) The ε phase gave a spectrum characteristic of a close-packed hexagonal lattice of side 2·718 Å and axial ratio 1·585.

(5) (*a*) The zinc-copper system crystallises on a rhombohedral hexagonal lattice from copper to γ brass, and on a close-packed hexagonal system from ε (or possibly δ) brass to zinc. The observed parameter of the lattice of ε brass suggests that the copper atom causes the zinc atom to rotate about an axis perpendicular to a $11\bar{2}0$ plane, until the zinc atoms in successive 0001 planes are separated by a distance equal to the side of the lattice of pure zinc. Fusion would then take place at about the same temperature in both cases.

(*b*) The very low value of the density previously ascribed to an alloy containing 10 per cent. copper is not confirmed. The value found for the density of this alloy is 7·35 grms./c.c. The observed density of the alloys examined is in good agreement with the value computed from X-ray data.

(*c*) The hardness of the brasses attains a maximum in the region of γ brass, where the atomic volume curve shows the greatest departure from the straight line joining the atomic volumes of copper and zinc. The hardness of the α phase is ascribed to local distortion and hat of the β phase to the difference in type of lattice. The relatively very great hardness of γ brass is due to small atomic volume and loss of symmetry.

(*d*) The fact that the atomic volume curve consists of two straight lines suggests the existence of an allotrope of zinc with an atomic volume of 13·92 Å^3. Consideration of the value of the parameter of the lattice of the β phase suggests that this phase is due to an allotropic modification of copper, with an atomic volume of 12·79 Å^3.

I. Introduction.

THE determination of crystal structure by means of X-rays provides a method of studying the constitution of metals and alloys which should yield valuable information concerning the changes which take place when we pass from one region of an equilibrium diagram to another. The method has been applied by the authors to the study of the zinc-copper series, and it is proposed in this Paper to give an account of the results so far obtained.

The observations of different metallurgists on this system of alloys are in general agreement, but there are differences of opinion as to certain details. Particularly is this so concerning the change which accompanies the thermal effect observed at 470°C. in the range of alloys containing 40 to 63 per cent. copper. In the early stages of the investigation on the zinc-copper series Roberts-Austen,* who was the first to observe the effect, attributed it to a eutectoid change. After the work of Shepherd† on the series, it was doubtful whether the effect actually occurred, as he failed to detect it. Later, however, Carpenter and Edwards‡ made a careful thermal analysis of the series proving beyond question the existence of the effect. They attributed it to the breaking down of the constituent into a mixture of α and γ. This explanation was disputed by Hudson,§ who brought evidence to show that the thermal effect observed was due to a polymorphic change of β to β'. Evidence in

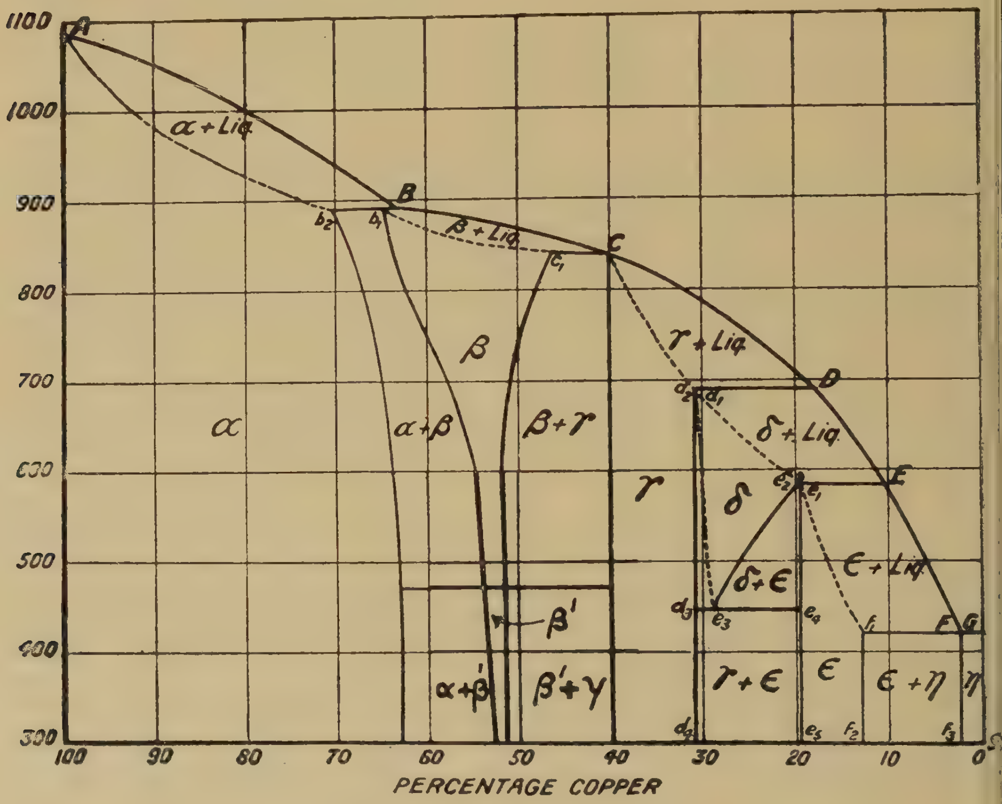


FIG. 1.

---

* Fourth Report to the Alloy Research Committee (1897).

† Jour. Phys. Chem. 8, p. 421 (1904).

‡ Jour. Inst. Metals, No. 1, p. 127 (1911).

§ Jour. Inst. Metals, No. 2, p. 89 (1914).

support of this conclusion has recently been published by Hiroshi Imai,* who employed the electric resistance method of measurement.

We have been able by the X-ray method to investigate this point in detail and, in addition, to carry out a general survey of the whole system. Owing to the complicated nature of the zinc end of the series (see Fig. 1), it is somewhat difficult to prepare some of the alloys in suitable form for X-ray measurement. Observations have, however, been made on the γ and ε phases in addition to the α, β and β'.

The zinc-copper alloys have already been examined by X-ray analysis by Bain†

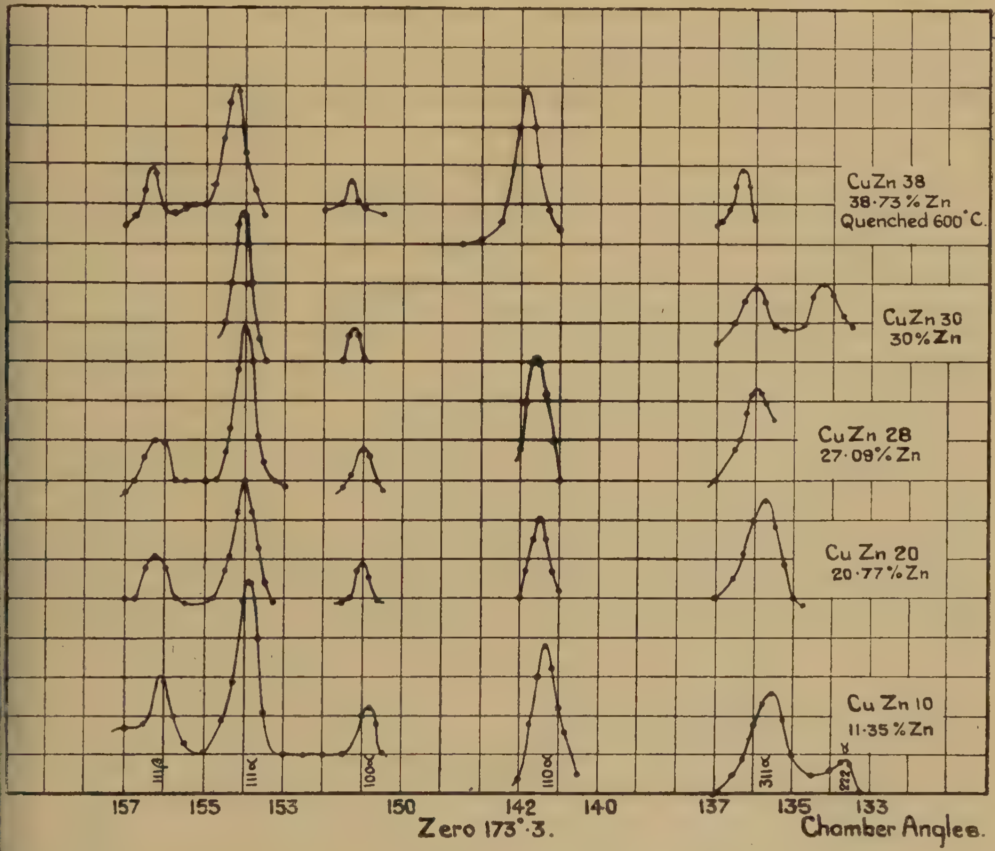


FIG. 2.

nd Mary Andrews.‡ Particular attention was paid by the former to the α phase, hilst the latter carried out a general survey of the whole series. In both cases the hotographic X-ray method of analysis was employed. For this method the material nder examination is usually reduced to a fine powder, a small quantity of which is placed in a tiny glass tube situated in the path of a monochromatic beam of X-rays.

---

* Science Reports, Tohoku Imperial University, Vol. 11, No. 5, p. 313 (1922).

† Chem. & Met. Eng., p. 663, Oct. 5 (1921) ; p. 21, Jan. 3 (1921) ; p. 65, Jan. 10 (1923).

‡ Phys. Rev., Vol. 21, p. 245 (1921).

In the present work a plate of the material under investigation is used and the reflections from crystal faces measured by the Bragg ionisation spectrometer. An account of the method of procedure has already been published by the authors.*

II. Results.

(1) *Alloys containing up to* 38·7 *per cent. Zinc by weight.*

These alloys, which constitute the a brasses, were prepared from chilled castings 1 in. in diameter, which had been annealed at 530 to 540°C. for 1 hour. The castings were rolled to a thickness of 0·25 in. and again annealed for 2½ hours at 550 to 600°C. Finally, they were rolled to a thickness of 0·125 in., annealed at 600°C. for 30 minutes and quenched in water. The specimens were polished and etched and presented a surface of at least 1 cm. square for examination by the X-ray spectrometer.

The results of the X-ray examination of five alloys containing up to 38·7 per cent. zinc are given in Table I. The actual observations are plotted in Fig. 2. All the alloys gave spectra characteristic of the face centred cubic structure of copper, the addition of the zinc causing an expansion of the lattice which is shown by the general shift of the lines in the spectra towards the origin as the amount of zinc is increased. The addition of 38·7 per cent. zinc alters the parameter of the copper lattice from 3·60 Å to 3·696 Å.

Table I.

Form.	11·35% Zn.		20·77% Zn.		27·09% Zn.		30% Zn.		38·73% Zn.	
	θ	a	θ	a	θ	a	θ	a	θ	a
111β	8°38′	3·634	8°33′	3·667	8°35′	3·656	—	—	8°30′	3·689
111α	9°42′	3·638	9°39′	3·667	9°39′	3·656	9°37′	3·666	9°33′	3·695
100α	11°14′	3·633	11° 8′	3·665	11°10′	3·656	—	—	11° 0′	3·710
110α	16° 0′	3·633	15°54′	3·653	15°51′	3·664	—	—	15°44′	3·691
311α	18°52′	3·629	18°47′	3·645	18°42′	3·660	18°39′	3·670	18°30′	3·699
222α	—	—	—	—	—	—	19°32′	3·667	—	—
Mean Values		3·633Å		3·657Å		3·658Å		3·668Å		3·696Å

Table II.

% Zn.	ρ (gms./c.c.)	M_s.	$\sqrt[3]{\frac{4M_s}{\rho}}$	a.	Diff.
0	8·93	63·57	3·608Å	3·605Å	—·003
11·35	8·80	63·78	3·629	3·633	·004
20·77	8·67	63·90	3·651	3·657	·006
27·09	8·57	64·06	3·667	3·658	—·009
30·0	8·54	64·19	3·673	3·668	—·005
38·73	8·43	64·29	3·694	3·698	·004

The figures in Table II. show that solution takes place by the substitution o a zinc atom for a copper atom. The average atomic weight M_s is computed from the composition of the alloy by use of the relation

---

* Proc. Phys. Soc., Vol., 35, Part 2, p. 101 (1923).

$$M_s=\frac{100}{\frac{x}{M_1}+\frac{100-x}{M_2}}$$

x being the percentage of zinc by weight, $M_1=65 \cdot 37$, and $M_2=63 \cdot 57$, being respectively the atomic weights of zinc and copper (O=16).

As will be seen from the table, the values of $\sqrt[3]{\frac{4M_s}{\rho}}$ do not differ from the observed values of a, the parameter of the lattice by as much as 0·25 per cent. These results are in agreement with the observations of the authors on other solid solutions which have already been published.*

(2) *Alloys containing* 48·5 *per cent. Zinc.*

The alloy containing 48·5 per cent. zinc lies in the region of β brasses. Two specimens were examined; the first specimen was heated for 10 minutes at 550°C. and quenched in water, the second specimen was heated for 5 minutes at 500°C, slowly cooled during half an hour to 450°C., quickly cooled to about 400°C., and then quenched in water. According to the constitutional diagram (Fig. 1), the first specimen should consist of the pure β phase, and the second specimen of either the pure β' phase or a mixture of the α and γ according to whether the view of Desch and of Hudson or that of Carpenter and Edwards is the correct one regarding the change which takes place at 470°C.

Two samples of the first specimen were examined and found to possess a spectrum corresponding with a centred cubic structure of side 2·950Å. This is in good agreement with the value of the parameter, 2·945Å, calculated from the observed density of the material. The sines of the angles of reflection for the two samples are given in Table III. In neither sample could we find an indication of the presence of a face centred lattice.

TABLE III.—48·5 *per cent. Zinc* (*Quenched from* 550°C.).

I.			II.		
Sin θ.	Form.	a.	Sin θ.	Form.	a.
0·1573	110β	2·832	0·1504	110β	2·962
0·1719	110α	2·912	0·1694	110α	2·954
0·2122	100β	2·969	0·2130	100β	2·957
0·2380	100α	2·974	0·2385	100α	2·968
0·2622	211β	2·943	0·2622	211β	2·943
0·2932	211α	2·956	0·2940	211α	2·949
0·3379	220α	2·962	0·3387	220α	2·955
0·3795	310α	2·949	0·3738	310α	2·994
0·3995	321β	2·949	0·4139	111α	2·961
0·4486	321α	2·951	0·4501	321α	2·942
Mean value	... ...	2·950			2·958Å

---

* Proc. Phys. Soc., October (1923).

$$\rho = 8{\cdot}32 \text{ grms./c.c.}$$

$$M_s = 64{\cdot}45 \times \frac{1{\cdot}663}{1{\cdot}008} \text{ grms.}$$

$$a(\text{calc.}) = \sqrt[3]{\frac{2M_s}{\rho}} = 2{\cdot}945\,\text{Å}$$

$$a(\text{obs.}) = 2{\cdot}950\,\text{Å}$$

The second specimen (two samples of which were examined) which had been slowly cooled to a temperature below 470°C. gave the results shown in Table IV. The spectrum is again characteristic of the centred cube and cannot be distinguished from that of the β phase. The similarity between the two spectra is evident from Fig. 3. The reflections of the K_α and K_β radiations from the 110 faces and of the K_α radiation from the 100 and 211 faces were carefully examined and gave a value 2·946 Å for the parameter. The observed density was the same as for β brass, which requires a parameter 2·945 Å. We conclude from these observations that there is no change of crystalline structure during the heat evolution observed at 470°C. According to the constitutional diagram suggested by Carpenter and Edwards, this brass should contain about 50 per cent. α and 50 per cent. γ. Although very careful examination was made of the regions of the spectrum in which lines belonging to a face centred cube of the required parameter should appear, no trace of any reflection could be detected in these regions. In case, however, the method was not sensitive enough to detect the presence of the α structure if it existed in the samples of β' brass examined, measurements were made on three alloys from a region a little removed from that of β'. They contained 43·7 per cent. zinc and were quenched from different temperatures. The first was annealed for 2 minutes at 750°C., the second annealed for 1 hour at 500°C., and the

TABLE IV.—48·0 *per cent. Zinc, annealed below* 470°C.

	I.		II.	
Form.	Sin θ.	*a*.	Sin θ.	*a*.
110β	0·1501	2·968 Å	0·1513	2·944 Å
110α	0·1691	2·959	0·1702	2·941
100β	0·2124	2·966	0·2147	(2·934)
100α	0·2393	2·957	0·2393	2·957)
211β	0·2613	2·953	0·2630	(2·934)
211α	0·2940	2·949	0·2948	2·941
220α	0·3404	2·941	0·3395	2·948
310α	0·3778	2·963		
321β	0·4011	2·939		
111α	0·4163	2·944		
321α	0·4601	2·942		
Mean value ...		2·953 Å		2·946 Å

$$\rho = 8{\cdot}32 \text{ grms./c.c.}$$

$$M_s = 64{\cdot}45 \times \frac{1{\cdot}663}{1{\cdot}008} \times 10^{-24} \text{ grms.}$$

$$a(\text{calc.}) = \sqrt[3]{\frac{2M_s}{\rho}} = 2{\cdot}945\,\text{Å}$$

$$a(\text{obs.}) = 2{\cdot}949\,\text{Å}$$

third annealed for 3 hours at 400°C., quenching in water in each case. According to the constitutional diagram (Fig. 1), the first of the above should contain pure β, the second a mixture of α and β, and the third a mixture of α and β'. The second and third should be indistinguishable, since the structures of β and β' are crystallographically identical.

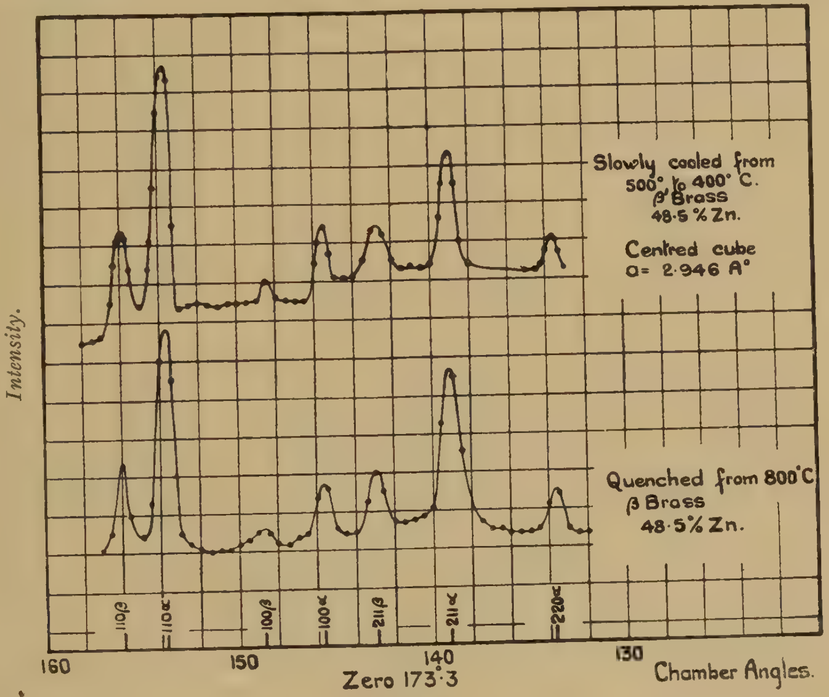


FIG. 3.

The results of the X-ray measurements on the second and third of the above specimens are shown in Tables V. and VI. respectively.

TABLE V.—*No. 45B. Annealed for 30 mins. at 500°C. 43·7 per cent. Zinc.*

2θ.	Sinθ.	α Brass.		β Brass.	
		Form.	a.	Form.	a.
17·5	0·1519			110β	2·932
19·1	0·1661	111α	3·690		
19·6	0·1707			110α	2·944
22·1	0·1918	100α	3·691		
24·8	0·2147			100β	2·934
27·9	0·2410	110β	3·697	100α	2·937
30·3	0·2613			211β	2·953
31·4	0·2706	110α	3·699		
34·4	0·2957			211α	2·932
35·3	0·3032			220β	2·939
37·0	0·3173	311α	3·699		
39·7	0·3395			220α	2·949
		Mean value ...	3·695Å		2·940Å

TABLE VI.—*No.* 45*C.* *Annealed for* 3 *hours at* 400°*C.* 43·7 *per cent. Zinc.*

2θ.	Sin θ.	α Brass.		β' Brass.	
		Form.	a.	Form.	a.
17·2	0·1495	111β	(3·649)	110β	2·980
19·1	0·1659	111α	3·695		
19·55	0·1696			110α	2·950
22·0	0·1908	100α	3·710		
27·9	0·2410			100α	2·937
30·5	0·2630			211β	2·934
31·1	0·2697	110α	3·711		
34·3	0·2948			211α	2·941
37·1	0·3181	311α	3·688		
39·8	0·3404			220α	2·941
		Mean value ...	3·701Å		2·941Å

In each case a mixture of the two constituents α and β or β' was observed. The remaining specimen gave a spectrum characteristic of a centred cube without any trace of the α constituent. The observations taken between chamber angles of 150° and 155° are plotted in Fig. 4. Those suffice to show the different appearance of the spectra, and the absence of reflections from the 100 and 111 faces of the α constituent in the spectra of specimen quenched from 750°C.

These observations show that if the α constituent were present in the alloy containing 48·5 per cent, zinc which had been annealed at a temperature below 470°C., it would have been detected in the analysis.

We therefore conclude from the results of the present investigation that the crystalline structure of the β and β' phases are identical both as regards type and dimension of lattice and that the thermal effect which occurs at 470°C. in alloys containing 48·5 per cent. zinc is not accompanied by the breaking up of the β constituent into a mixture of α and γ.

(3) *Alloy containing* 67·2 *per cent. Zinc.*

Alloys containing 60 to 70 per cent. zinc form the region of γ brasses. The specimens examined were annealed for 2 hours at 500°C. and quenched in water. The X-ray reflections were found to be very weak, the five specimens which were examined all suffering from this defect. With only a limited number of lines available, the solving of the structure presented some difficulty.

In the initial examination of the spectrum five lines could be detected with certainty—three of these being K_α reflections and two K_β. The α-lines occurred at angles 19·7°, 27·8° and 34·6°, the sines of half these angles being in the ratio :—

$$0{\cdot}1713 : 0{\cdot}2402 : 0{\cdot}2974 = 1 : \sqrt{1{\cdot}96} : \sqrt{3{\cdot}02}$$

or very nearly as $1 : \sqrt{2} : \sqrt{3}$, which are the ratios required for the sines of the angles of reflection from the 100, 110 and 111 planes of a simple cube, or from the 110, 100 and 211 planes of a centred cube. Assuming that the alloy has a simple cubic structure and taking M, the average atomic mass to be $\dfrac{64{\cdot}77 \times 1{\cdot}663}{1{\cdot}008} \times 10^{-24}$.

grms., the density is calculated to be 12·06 grms./c.c.—an impossible value. On the alternative assumption that the structure is a body centred cube of side 2·92 Å, the calculated density becomes 8·60 grms./c.c. The observed density is 8·0 grms./c.c. this figure being the mean of several determinations carried out on different specimens and by different methods, including weighing the powdered material in paraffin as water was found to attack the alloy. The figure 8·0 grms./c.c. is the density to be expected from an alloy of this composition from the density curve in Fig. 5. The disagreement between the calculated and observed density is about 7½ per cent. This would require an error of 2½ per cent. in the value of the parameter—a discrepancy which is too great to be due to experimental error. With a view to fixing the parameter with greater certainty, a detailed survey of the spectrum was made in the region of the second order reflection of 110α the most intense line of the spectrum. A reflection of small intensity at an angle of 40·2° was found, the corresponding sine being 0·3437, which is in good agreement with the value 0·1713, previously found for the sine of the angle of the 1st order reflection. The error is, therefore, not in the measurement of the parameter and a structure other than the centred cube must be found to account for the observed density of the alloy.

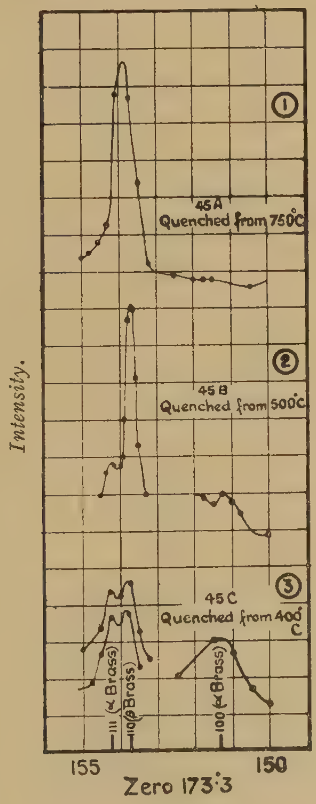


FIG. 4.

An alternative structure was found in a close-packed hexagonal lattice of side 2·92Å and axial ratio 1·225, the $10\bar{1}1$, $11\bar{2}0$ and $20\bar{2}1$ planes providing reflection with the sines of the angles in the ratio $1 : \sqrt{2} : \sqrt{3}$. In this case the calculate density 8·1 grms./c.c. was in close agreement with the observed value. Th difficulty encountered with this structure was that the $10\bar{1}0$ line, which should b present, was missing, and a close examination of the spectrum in this region faile to reveal its presence.

In view of the uncertainty as to the type of lattice present, an additional numbe of specimens was examined and the reflections recorded in Table VII., though c small intensity, were found to be present.

TABLE VII.—*γ Brass. Rhombohedral Hexagonal.*

2θ.	Sin θ.	Form.	d.	a ($c=0{\cdot}6495$).
17·4	0·1513	$11\bar{2}0\beta$	$a/2$	4·163Å
19·1	0·1662	$10\bar{1}1\alpha$	$a\Big/\sqrt{\frac{4}{3}+\frac{1}{c^2}}$	4·100
19·7	0·1713	$11\bar{2}0\alpha$	$a/2$	4·130
27·8	0·2402	$20\bar{2}1\alpha$	$a\Big/\sqrt{\frac{16}{3}+\frac{1}{c^2}}$	4·090
28·6	0·2470	$10\bar{1}2\beta$	$a\Big/\sqrt{\frac{4}{3}+\frac{4}{c^2}}$	4·194
30·5	0·2630	$10\bar{1}0\beta$	$a/2\sqrt{3}$	4·148
32·8	0·2823	$10\bar{1}2\alpha$	$a\Big/\sqrt{\frac{4}{3}+\frac{1}{c^2}}$	4·123
34·1	0·2932	$21\bar{3}1\alpha$	$a\Big/\sqrt{\frac{28}{3}+\frac{1}{c^2}}$	4·130
34·6	0·2974	$10\bar{1}0\alpha$	$a/2\sqrt{3}$	4·121
38·0	0·3265	$20\bar{2}2\alpha$	$a\Big/2\sqrt{\frac{4}{3}+\frac{1}{c^2}}$	4·185
40·2	0·3437	$22\bar{4}0\alpha$	$a/4$	4·118
			Mean ...	4· 36Å

$$c=0{\cdot}6495$$

$$a=4{\cdot}136\times10^{-8}\text{ cm.}$$

$$M_s=64{\cdot}77\times\frac{1{\cdot}663}{1{\cdot}008}\times10^{-24}\text{ grms.}$$

$$\rho=\frac{6M_s}{\sqrt{3}a^3c}=8{\cdot}06\text{ grms./c.c.}$$

$$\rho(\text{obs.})=8{\cdot}00\text{ grms./c.c.}$$

These figures do not agree with the reflections to be expected from the hexagona lattice considered above, but may be accounted for by a rhombohedral lattice c side 4·136Å and axial ratio 0·6495—a structure which requires a density c 8·06 grms./c.c. in agreement with observation. The centred cubic structure considere above which failed to account satisfactorily for the observed density is equivalen to a rhombohedral lattice of side 4·13Å and axial ratio 0·6125, while β brass is centred cube of side 2·946, i.e., a rhombohedral structure of side 4·16 and axia ratio 0·6125 $\left(=\frac{\sqrt{3}}{2\sqrt{2}}\right)$. The structure here assigned to γ brass is not very different from either of these, but the change in axial ratio reduces the number of trigonal axes of symmetry from four for the cubic structure to one for the rhombohedral.

It is hoped to continue the investigation of the structure of this material using specimens of different compositions throughout the range of the γ phase.

Alloy containing 80·1 *per cent. Zinc.*

This specimen of ε brass was annealed for five hours at 550°C. before quenching in water. X-ray analysis yielded a spectrum, the details of which are included in Table VIII. The structure which satisfactorily fits the experimental observations is a closed packed hexagon of axial ratio 1·585 and parameter 2·718 Å. The observed and calculated densities are respectively 7·6 grms. per cubic centimetre and 7·8 grms. per cubic centimetre, which show fair agreement.

TABLE VIII.—*Brass,* 80·09 *per cent. Zinc. Annealed* 5 *hours at* 550°*C.*

2θ.	Sin θ.	Close packed hexagonal.		a (c=1·585).
		Form.	d.	
17·3	0·1504	$10\bar{1}0\alpha$	$\frac{a\sqrt{3}}{2}$	2·718
19·0	0·1650	0001α	$\frac{ac}{2}$	2·707
19·7	0·1711	$10\bar{1}1\alpha$	$a\Big/\sqrt{\frac{4}{3}+\frac{1}{c^2}}$	2·724
25·6	0·2215	$10\bar{1}2\alpha$	$a\Big/\sqrt{\frac{4}{3}+\frac{4}{c^2}}$	2·733
30·0	0·2588	$11\bar{2}0\alpha$	$a/2$	2·735
31·8	0·2740	$11\bar{2}2\beta$	$a\Big/\sqrt{4+\frac{4}{c^2}}$	2·718
33·7	0·2898	$10\bar{1}3\alpha$	$a\Big/\sqrt{\frac{4}{3}+\frac{9}{c^2}}$	2·708
35·8	0·3074	$11\bar{2}2\alpha$	$a\Big/\sqrt{4+\frac{4}{c^2}}$	2·723
38·4	0·3289	0002α	$\frac{ac}{4}$	2·715
40·3	0·3445	$20\bar{2}2\alpha$	$a\Big/2\sqrt{\frac{4}{3}+\frac{1}{c^2}}$	2·704
42·5	0·3624	$10\bar{1}4\alpha$	$a\Big/\sqrt{\frac{4}{3}+\frac{16}{c^2}}$	2·710
			Mean ...	2·718Å

$$a=2{\cdot}718\times10^{-8}\text{ cm.}$$

$$c=1{\cdot}585$$

$$M_s=64{\cdot}97\times\frac{1{\cdot}663}{1{\cdot}008}\times10^{-24}\text{ grms.}$$

$$\rho=\frac{4M_s}{\sqrt{3}\,.\,a^3c}=7{\cdot}77\text{ grms./c.c.}$$

$$\rho(\text{obs.})=7{\cdot}6\text{ grms./c.c.}$$

III. CONCLUSIONS.

(1) *Atomic Structure.*

The results obtained by X-ray analysis of the zinc-copper system summarised in Table IX. are in agreement with the constitutional diagram of Shepherd as modified by Desch and Hudson. The figures quoted in the table for zinc are due to Hull.*

TABLE IX.

Phase.	Composition.		Structure.	Parameter.	Axial ratio.
	Atomic % zinc.	% zinc by weight.			
Cu	0·0	0·0	Face centred cubic	3·608Å	
α	11·07	11·35	,,	3·629	
α	20·27	20·77	,,	3·651	
α	26·54	27·09	,,	3·667	
α	29·42	30·0		3·673	
α	38·05	38·73	,,	3·692	
β	47·95	48·5	{Centred cubic {Rhombohedral hexagonal	2·946 4·17	— 0·6125}
β′	47·95	48·5	Ditto	4·17	0·6125
γ	66·6	67·2	Rhombohedral hexagonal	4·136	0·649
[δ	75·0	75·5	Closed packed hexagonal	2·776	1·475]
ε	79·5	80·1	,,	2·718	1·585
Zn	100·0	100·0	,,	2·670	1·860

The changes which occur in the lattice are perhaps most easily visualised by remembering that a face centred cube of side a is equivalent to a rhombohedral lattice of side $a/\sqrt{2}$ and axial ratio $\sqrt{6}$. Thus the copper lattice is a rhombohedral one of side 2·54Å and height $2{\cdot}54 \times \sqrt{6} = 6{\cdot}23$Å, successive (0001) planes of copper following one another at intervals of $\frac{6{\cdot}23}{3} = 2{\cdot}08$Å. The addition of 38 atomic per cent. zinc expands the rhombohedral lattice to one of side 2·62Å and height 6·41Å, the axial ratio remaining unchanged. The centred cubic lattice of the β brasses is equivalent to a rhombohedral lattice of side 4·17Å, i.e., $a\sqrt{2}$, and axial ratio $\frac{\sqrt{3}}{2\sqrt{2}}$ so that the height of the unit hexagonal prism is 2·55Å. Thus, from this point of view the difference between the α, β and γ brasses is not one of difference of type of lattice, but only of relative dimensions. The side of the hexagonal prism increases from 2·62Å for an α brass containing 38 atomic per cent. zinc, to 4·17Å for a β brass containing 48 atomic per cent. zinc. The difference between the β and γ brasses is much less marked as far as the dimensions of the lattice are concerned, the axial ratio increasing from 0·6125 to 0·649 and the side of the hexagonal prism decreasing from 4·17Å to 4·13Å. The structure in this case, however, loses symmetry, the cubic lattice of the α and β phases having four trigonal axes of symmetry, while the rhombohedral lattice of the γ phase has only one.

Passing on from the γ to the ε region, the lattice changes from rhombohedral to hexagonal close packed, which is also the lattice of pure zinc. For ε brass the side of the hexagonal prism is 2·72Å and the height 4·31Å, and for pure zinc the corresponding figures are 2·67Å and 4·97Å.

---

* Phys. Rev., Vol. 17, p. 571 (1921).

It appears, then, that we may regard the zinc-copper alloys as being built on two hexagonal lattices, those between copper and γ brass following the rhombohedral and those between zinc and ε brass (or possibly δ brass) following the hexagonal closed packed arrangement.

The spectral curves do not supply sufficient information to enable us to place the atoms in their respective positions in the lattice. The difficulty is enhanced owing to the fact that zinc and copper are of so nearly equal atomic weights. We may, however, be allowed to direct attention to certain points of interest in connection with some of the lattices. If we follow Hull and assume that zinc atoms are prolate spheroids, which in pure zinc are arranged with their circular sections parallel to the 0001 planes and their major axes perpendicular to these planes, then the closest distances of approach of the atoms are 2·67Å and 2·92Å, the former being the side a of the hexagonal lattice and the latter the quantity $a\sqrt{\frac{c^2}{4}+\frac{1}{3}}$. In ε brass $a=2{\cdot}72$Å and $c=1{\cdot}585$, so that $a\sqrt{\frac{c^2}{4}+\frac{1}{3}}=2{\cdot}67$Å, the diameter of the circular section of the zinc atom. This suggests that the presence of the copper atoms causes the zinc atoms to rotate about an axis perpendicular to a set of (1120) planes, thus preserving the closest distance of approach between zinc atoms which obtains in the pure zinc lattice. We might, therefore, expect that the forces of cohesion would fail to be sufficient to maintain the zinc atoms in contact at about the same temperature for zinc and for ε brass. It is of interest to note that, according to the constitutional diagram of Shepherd, brass containing about 13 per cent. copper (at the end of the ε region rich in zinc) begins to melt at a temperature sensibly the same as the melting point of zinc.

The atomic proportion of copper to zinc in ε brass is as 1 to 7. Atoms in this proportion can be fitted into a hexagonal closed packed lattice with very little distortion if we assume the (0001) planes to consist alternately of zinc atoms and of copper and zinc atoms in the ratio of 1 to 3. In the latter planes the copper atoms would take up their positions on a hexagon of side $2a$, the zinc atoms occupying the remaining positions.

In δ brass the ratio of the number of copper atoms to the number of zinc atoms is 1 to 3. If it be assumed that the lattice is close-packed hexagonal, the average mass (M_s) associated with each point in the lattice will be $64{\cdot}92\times\frac{1{\cdot}663}{1{\cdot}008}\times10^{-24}$ grms. The density of the material deduced from the observed curve of density in Fig. 5 is 7·84 grms. per c.c.; so that the average atomic volume $\left(\frac{M_s}{\rho}\right)$ is 13·2 cubic Ångstroms. If the addition of the necessary number of copper atoms to ε brass to produce δ brass causes a further rotation of the zinc atoms (such as was assumed in connection with the change from zinc to ε brass) so that the major axes of the zinc atoms fall along the sides of the hexagon joining two copper atoms, the side of the hexagon becomes 2·776Å. In this case the axial ratio $\left(c=\frac{4M_s}{\sqrt{3}a^3\rho}\right)$

works out to be 1·475. On this arrangement the closest distance of approach of zinc and copper atoms in the $(11\bar{2}0)$ plane will be 2·604 Å, which is in close agreement with the sum of the radius of the copper atom (1·274 Å) and the minor axis of the zinc atom (1·335 Å). We were unable in the present investigation to make any direct measurements on δ brass, owing to its being unstable at ordinary temperatures. The hexagonal close-packed structure suggested here is a possible one, but the evidence in support of it is incomplete, and further work is necessary to establish it.

(2) *Density.*

The values of the densities calculated from the results of the X-ray analysis of the α, β, γ and δ phases are in good agreement with the observed values of the densities. Previous work on the densities of zinc-copper alloys carried out by Bamford* is in agreement with the results recorded here for alloys up to 60 per cent. zinc ; for alloys of higher zinc content, however, there is disagreement. Bamford records a very low density (6·8 grms. per c.c.) for a brass containing about 10 per cent. copper by weight. This is in the $(\varepsilon+\eta)$ region, and on this account we were unable to make a determination of the density by direct X-ray measurement. It was considered that an independent observation of the density would, however, be desirable. A 1 in. chill casting weighing about 1 kg. and containing 10·2 per cent. copper by weight was accordingly prepared. A piece weighing about 100 grammes was sawn off the lower end of the casting and gave a density of 7·35 grms. per c.c. This value is about that to be expected from the constitutional diagram, because in this region the metal exhibits a duplex structure, being a mixture of the ε and η phases, and the specific volume of the material will be the sum of the specific volumes of the constituent phases taken in the proper proportions. We conclude, therefore, that the low value of the density of brass containing 10 per cent. copper given by Bamford is not the true crystal density.

It is probable that the directly observed densities of the alloys containing 76, 80 and 90 per cent. zinc are on the low side, as the materials were distinctly porous, so that the figure obtained from the X-ray data for ε brass may be nearer the true density than the smaller directly observed value, in spite of the fact that the experimental error in the value of the parameter is trebled in the computation of the density. The density-composition curve (Fig. 5) has accordingly been provisionally drawn between the two values of the density observed for the alloy containing 80 per cent. zinc. This brings the whole curve in this region slightly above the observed values of the densities.

(3) *Hardness.*

The atomic volume curve shown in Fig. 5 consists very approximately of two straight lines meeting in the region of the γ brass.† We have at present no evidence to show what changes of atomic volume take place within the regions of phases other than the α phase, and have drawn a smooth curve through the determined points.

The γ brasses lie in the region where there is the greatest departure of the curve rom the straight line joining the atomic volumes of copper and zinc. This implies hat there is here a maximum of distortion, the atoms "sharing electrons" or eing "compressed," so that they occupy a smaller volume than in either of the pure netals. Assuming that the hardness of a material, that is, its resistance to slip, lepends upon the amount of distortion obtaining,* we should expect that the hardness of the zinc-copper alloys would increase from the copper end to the region of γ brass, and then diminish as we proceed to the zinc end of the series. This conclusion s supported by experiment. The results of Murray† on the hardness of the brasses, as measured by the Shore Sceleroscope, show that β brass is about twice as hard as

---

* Bamford, Jour. Inst. Metals.

† The intersection occurs at 68 per cent. zinc, or very nearly $CuZn_2$. It is doubtful whether the inference that a compound of this composition exists is justified. (*Cf.* Desch, "Intermetallic Compounds," p. 40. Longmans, Green, 1914.)

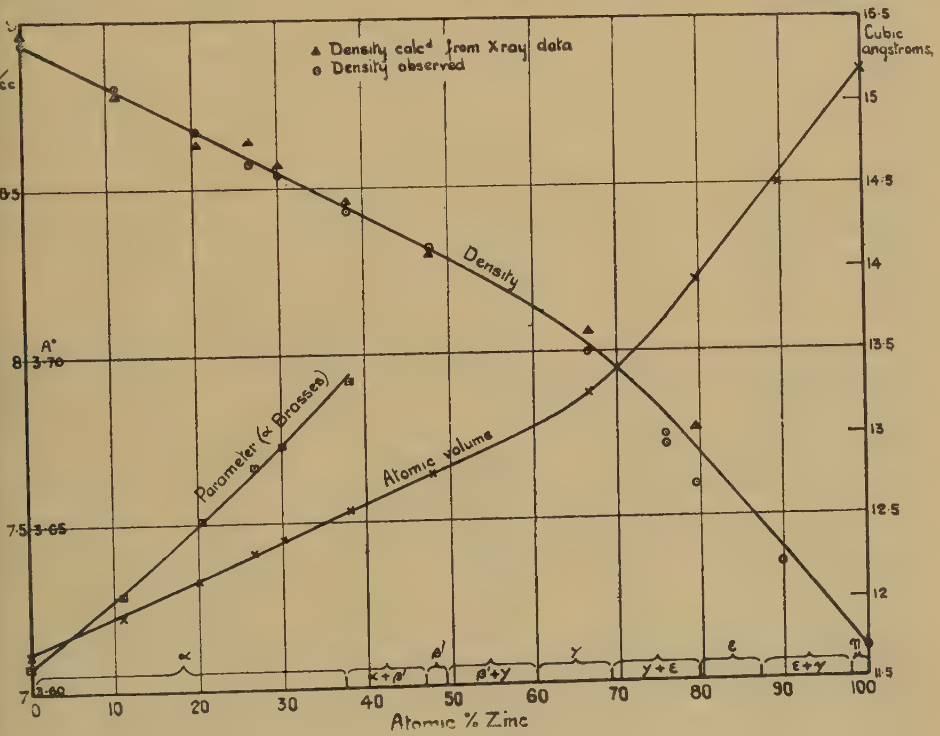


FIG. 5.

pure copper, and that γ brass is about four times as hard as β brass, while ε brass is of about the same hardness as β brass.

There is yet another point of interest which may be considered in reference to the hardness of these alloys. It has been found that the a phase is face centred cubic, and the β phase centred cubic. If we suppose that slipping takes place on the hexagonal (0001) planes, there would be more resistance offered to slip on these planes in the centred than in the face centred cubic lattice, and so on this account alone the β phase would be harder than the α phase. With regard to the relative hardness of β and γ brasses, the former has four axes of trigonal symmetry, whereas the latter has only one. This loss of symmetry coupled with the fact that in γ brass we have the maximum amount of distortion will probably account for the great hardness of γ brass as compared with the hardness of the other alloys in the series.

---

* There is ample experimental evidence that hardness is closely related to atomic or molelar volume. For instance it has been observed that a series of isomorphous chemically similar substances exhibit degrees of hardness inversely proportional to their molecular volume. (*See* A. E. H. Tutton, Crystallography, Vol. 1, p. 536.)

† M. T. Murray, Jour. Inst. Metals, No. 2, Vol. 2, p. 199 (1909).

The increase of hardness of alloys in the α phase with increasing zinc content is accounted for by the local distortion caused by the introduction of the atoms of zinc into the copper lattice.* The same explanation obtains for the relative hardness of zinc, η and probably ε brass.

(4) *Allotropy.*

We have observed that the atomic volume curve may be considered in two parts represented by straight lines meeting in the region of γ brass. Along the one limb the crystal structure of the alloys follows the rhombohedral arrangement, whilst they follow the closed packed hexagonal arrangement along the other. If the atoms of copper and zinc existed in the brasses without loss of volume, the average atomic volume would be the straight line joining the atomic volume of copper, and the atomic volume of zinc. If we produce the line representing the atomic volume of the α and β phases, it will meet the zinc ordinate of the graph at a point which will give an atomic volume of 13·92Å^3. This hypothetical zinc atom, when mixed with different proportions of copper, will cause the average atomic volume to increase proportionately to the amount of zinc present.†

If we assume that this atom crystallises on a face centred lattice, the parameter will be 3·82Å and the closest distance of approach of the atoms will be 2·70Å. This is 1 per cent. greater than the minor diameter of the zinc atom. It would therefore appear that the zinc atom, when it is associated with copper atoms up to a concentration of that of γ brass, behaves as a sphere of radius 1·35Å.

If we assume that the prolate spheroidal shape of the ordinary zinc atom is due to the presence of the two valence electrons, then it would appear that when zinc is added to copper the latter deprives the zinc of these electrons, adding them to its own in the endeavour to form a stable ring.

One, if not two, allotropic modifications of zinc have been observed,‡ and it has been stated that a cubic form has also been noticed.

Rosenhain§ has suggested that the β and γ phases of the copper zinc system are due to an allotropic modification of copper, and it is to be observed that the cubic diagonal of the β brass lattice is exactly equal in length to the diagonal of the face of the cube in the lattice of pure copper. That is to say that spheres of the size of copper atoms could be packed into the lattice of β brass without any distortion, but would require to be held in position by external constraints or a rearrangement of the atomic field of force. The atomic volume of copper (diameter of atom,

---

* *See* W. Rosenhain, Proc. Roy. Soc., A., Vol. 99 (1921), and Trans. Amer. Inst. Mining and Metallurgical Engineers (1923).

† *Cf.* Nernst Theoretical Chemistry, p. 127. (Macmillan, 1923.)

‡ Miss K. E. Bingham, Jour. Inst. Metals, Vol. 2, p. 333 (1920).

§ Inst. of Metals, May Lecture (1923).

=2·552Å) is in the face centred state $V=\frac{1}{4}(D\sqrt{2})^3=11{\cdot}74$Å^3, and in the body
entred state $V'=\frac{1}{2}\left(\frac{2D}{\sqrt{3}}\right)^3=12{\cdot}79$Å^3. The atomic volume thus increases by 1·05Å^3,
hile the volume of the supposedly spherical atom is in both cases $\frac{4}{3}\pi\left(\frac{D}{2}\right)^3=8{\cdot}67$Å^3.
he zinc atom has been considered to be a prolate spheroid of semi-axes $r_1=1{\cdot}335$
nd $r_2=1{\cdot}502$Å, so that the volume of this atom is $\frac{4}{3}\pi r_1^2 r_2=11{\cdot}21$Å^3. Taking the
ompressibility of copper to be $0{\cdot}54\times10^{-6}$ per megabar, a tension of $16{\cdot}5\times10^4$ mega-
ars would be required to increase its volume from 11·74 to 12·79. A pressure of
nis magnitude applied to zinc (compressibility $1{\cdot}4\times10^{-6}$ per megabar) would
educe a volume of 11·21Å^3 to 8·62Å^3, which is almost exactly the volume at its
sposal in *β* brass.

We wish to express our best thanks to Dr. Rosenhain and the staff of the Metal-
rgy Department for helpful advice throughout the course of the investigation
e are particularly indebted to Miss G. W. Ford, B.Sc., of the Metallurgy Depart-
ent, for her most competent assistance in the preparation of the specimens.

DISCUSSION.

Dr. H. WEISS congratulated the authors on their work, and said that some of the results
tained by previous workers in the same field were palpably absurd. In some cases the diagrams
tained by X-ray analysis have borne no relation to those obtained by thermal and micro-
opical analysis ; for instance, they have shown only one kind of lattice in regions where the
evious methods clearly show two kinds of crystals. It was to be expected that X-ray methods
metallurgy would add to previously existing knowledge, but that they should contradict
does not inspire confidence in the school of workers who have hitherto pursued them. In
ew of these contradictions the authors' work is the first of its kind calculated to inspire confi-
nce in the minds of metallurgists. As regards the transformation of *β* brass into *β′*, the con-
usions reached by the authors can hardly be regarded as final, for it is impossible to be certain
at the structure of the *β* phase, which is only stable above 470°C., is retained by the act of
enching. Conclusive results on this head can only be obtained by direct measurements at the
gher temperatures. It is likely that X-ray analysis will throw much light on the causes which
ve rise to the series of solid solutions, *α*, *β*, *γ*, *δ*, *ε*, *η*, but probably no useful theory can be
med until a large number of experimental determinations have been made for various other
ies. In Sir Wm. Bragg's laboratory the speaker had begun a study of the same subject by a
otographic method. In the preliminary tests two kinds of samples were used : Those with
ry small crystals, which give well-defined but somewhat diffuse lines, were valuable in giving a
eral idea of the spectrum, while those with larger crystals, which give fine and clearly separated
es, were preferable for obtaining exact measurements. Samples were also submitted to an
istant in the laboratory who was skilful in the use of the ionisation chamber, but for the 111
ne of copper he was only able to obtain a deflection in his electroscope of eight divisions in
0 of a second, as compared with a deflection of 6 divisions for the troughs of the intensity
ves in the same neighbourhood. The conditions seemed therefore very unfavourable for
ermining the peaks of these curves. Could the authors give some particulars as to their
nique in this connection ?

Mr. T. SMITH referred to the comparison made by Dr. Owen, in presenting the Paper, between
volume elasticity of the alloys as measured in the ordinary way, and the forces acting upon
ms during strain. It did not seem safe to argue directly from one of these quantities to the
ier.

Dr. E. A. OWEN, in reply to the discussion, thanked Dr. Weiss for his kind remarks. With
d to his reference to the results obtained with *β* brass, the investigation undoubtedly proved
osence of the *α* phase in a copper-zinc alloy containing 48 atomic per cent. zinc, annealed as

described in the Paper and quenched from 400°C. This would not be the case if the evolution of heat associated with the temperature 470°C. were accompanied by the splitting up of the β phase into the two constituents α and γ. He agreed that it would be desirable to investigate the structure of alloys at high temperatures, and they (the authors) hoped to be in a position to make such measurements in the near future.

In regard to the intensity of the peaks in the spectral curves, these varied according to the specimens examined. The intensities of reflections from planes rich in atoms were easily measurable. Small deflections could also be detected and measured with certainty after a little practice. For this work the speaker emphasised the necessity of maintaining a steady condition of discharge of the X-ray bulb. The reflections obtained with metals in the form of plates as used in the investigation were not as a rule as intense as those obtained with single crystals. It was pointed out that this was not a serious drawback in view of the fact that the sensitive region of the scale of the tilted electroscope is limited. The definition of the peaks in the spectral curves is such that in general the maxima can be fixed to a few minutes of arc.

As regards Mr. T. Smith's criticism, Dr. Owen said that they (the authors) had thrown out some tentative suggestions at the end of their Paper chiefly as indications of the lines of inquiry to be followed. The assumptions made were admittedly hypothetical, but on these assumptions the numerical results obtained from considerations of volume elasticity fitted in well with the results of the X-ray analysis.

PUBLICATIONS OF THE PHYSICAL SOCIETY.

THE SCIENTIFIC PAPERS
OF THE LATE
SIR CHARLES WHEATSTONE, F.R.S.
Demy 8vo, cloth. Price 12s.; to Fellows, 6s.

Uniform with the above.

THE SCIENTIFIC PAPERS OF
JAMES PRESCOTT JOULE, D.C.L., F.R.S.
Vol. I. 4 Plates and Portrait, price 18*s.*; to Fellows, 9*s.*
Vol. II. 3 Plates, price 12*s.*; to Fellows, 6*s.*

PHYSICAL MEMOIRS.

RT I.—Von Helmholtz, On the Chemical Relations of Electrical Currents. Pp. 110. *Price 6s.; to Fellows, 3s.*

RT II.—Hittorf, On the Conduction of Electricity in Gases; Puluj, Radiant Electrode Matter. Pp. 222. *Price 12s.; Fellows, 6s.*

RT III.—Van der Waals, On the Continuity of the Liquid and Gaseous States of Matter. Pp. 164. *Price 12s.; to Fellows, 6s.*

REPORT ON RADIATION AND THE QUANTUM THEORY.
By J. H. JEANS, D.Sc., LL.D., F.R.S.
Second Edition Now Ready.—*Price 7s. 6d. Bound in Cloth.*

REPORT ON THE RELATIVITY THEORY OF GRAVITATION.
By A. S. EDDINGTON, M.A., M.Sc., F.R.S.
Plumian Professor of Astronomy and Experimental Philosophy, Cambridge.
Third Edition.—*Price 6s.; to Fellows, 3s. Bound in cloth, 8s. 6d.; to Fellows, 6s.*

REPORT ON SERIES IN LINE SPECTRA.
By A. FOWLER, F.R.S.,
Professor of Astrophysics, Imperial College of Science, South Kensington, London.
Price to Non-Fellows, 12s. 6d.; to Fellows, 6s. 3d. Bound in Cloth, 15s., to Fellows, 9s.

THE TEACHING OF PHYSICS IN SCHOOLS.
Price to Non-Fellows, 1s. 6d. net, post free 1s. 8d.

METROLOGY IN THE INDUSTRIES.
Price to Non-Fellows, 1s. 6d. net, post free 1s. 8d.

DISCUSSION ON LUBRICATION.
Price to Non-Fellows, 1s. 6d. net, post free 1s. 8d.

DISCUSSION ON ELECTRIC RESISTANCE. *Price 2s. 6d. net.*

DISCUSSION ON HYGROMETRY. *Price 5s. net.*

PROCEEDINGS.

e "Proceedings" of the Physical Society can be obtained at the following prices:—

Vol. I. (3 parts) bound cloth, 22*s.* 6*d.*
Vols. II., IV., V., XXIII., XXV., XXVI., XXVII., XXVIII., XXIX., XXX. & XXXI. (5 parts each), cloth, 34*s.* 6*d.*
Vols. III., VI. to XII. & XXII. (4 parts each), bound cloth, 28*s.* 6*d.*
Vol. XIII. (13 parts, each containing Abstracts), bound cloth (without Abstracts), 70*s.* 6*d.*
Vols. XIV. & XV. (12 parts, each containing Abstracts), bound cloth (without abstracts). 34*s.* 6*d.*
Vols. XVI. & XIX. (8 parts each), bound cloth, 52*s.* 6*d.*
Vols. XVII., XVIII. & XXI. (7 parts each), bound cloth, 46*s.* 6*d.*
Vols. XX. & XXIV. (6 parts), bound cloth, 40*s.* 6*d.*

Most of the parts can be purchased separately, price 6*s.*, by post 6*s.* 3*d.* Fellows can obtain *Proceedings* (in parts) for their personal use at half the above prices.

ABSTRACTS OF PHYSICAL PAPERS FROM FOREIGN SOURCES.
Vols. I. (1895), II. (1896), III. (1897), 22*s.* 6*d.* each; Fellows, 11*s.* 3*d.*

Strong cloth cases for binding the "Proceedings," price 3s. 6d. each, post free.

AKESLEY, T. H. A Table of Hyperbolic Sines and Cosines. *Price 2s. 3d.; to Fellows, 1s. 2d.*

FELDT, R. A. A List of Chief Memoirs on the Physics of Matter. *Price 3s.; to Fellows, 1s. 6d.*

Applications for the above Publications should be sent direct to
FLEETWAY PRESS, LTD.,
3-9, Dane Street, High Holborn, London, W.C.1

CONTENTS.

PAGE

Portrait of Alexander Russell, M.A., D.Sc., President 1922-24. *Frontispiece*

Report of Lecture: The Excitation and Ionization Potentials of Gases and Vapours. By FRANK HORTON, Sc.D., F.R.S. 1

I. X-ray Analysis of Solid Solutions. By E. A. OWEN, M.A., D.Sc., and G. D. PRESTON, B.A., The National Physical Laboratory 14

Discussion on The Structure of Sodium Salts. By S. H. PIPER, D.S.O., B.Sc., F.Inst.P., and E. N. GRINDLEY, B.Sc. 31

II. Scattering of Light by Carbon Dioxide, Nitrous Oxide and Some Organic Vapours. By A. L. NARAYAN, M.A., A.Inst.P. 32

III. On the Measurement of the Surface Tension of a Small Quantity of Liquid. By ALLAN FERGUSON, M.A., D.Sc. 37

Demonstration of Experiments on the Reproduction of Vowel Sounds. By Sir RICHARD PAGET, Bt. 4

IV. X-ray Analysis of Zinc-Copper Alloys. By E. A. OWEN, M.A., D.Sc., and G. D. PRESTON, B.A. 4